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NEW ANALYSES OF LEPIDOLITES AND THEIR INTERPRETATION*

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ABSTRACT

Seventeen new analyses of lepidolites are presented. These analyses seem to be in agreement with the structural requirements of micas, as revealed by the x -ray studies of other investigators. The analyses indicate that the rare alkalis, rubidium and cesium, are normal constituents of lepidolites.

The interpretation of a new analysis of polyolithionite, an end member of the lepidolite series, shows it to approximate closely the formula $\text{K} \cdot \text{Li}_2\text{Al} \cdot \text{Si}_4\text{O}_{10}\text{F}_2$. Columbium and titanium seem to be normal constituents of lepidolites near polyolithionite in composition.

The composition of the seventeen lepidolites closely approximates that of isomorphous mixtures of polyolithionite $[\text{K} \cdot \text{Li}_2\text{Al} \cdot \text{Si}_4\text{O}_{10}\text{F}_2]$ with biotite $[\text{K} \cdot \text{R}''_3 \cdot \text{AlSi}_3\text{O}_{10}(\text{OH}, \text{F})_2]$,

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lithium muscovite $[K_4 \cdot Li_6Al_6 \cdot Al_4Si_{12}O_{40}(OH, F)_8]$, and muscovite $[K \cdot Al_2 \cdot AlSi_3O_{10}(OH, F)_2]$. The selection of biotite as an end member is arbitrary and other end members may be taken to account for the bivalent ions present.

Evidence is presented indicating discontinuous isomorphism. Theoretical consideration of this evidence suggests the following formulas for lepidolites: ideal formula A, $K \cdot Li_2Al \cdot Si_4O_{10}F_2$, the formula of polyolithionite; ideal formula B, $K_4 \cdot Li_6Al_6 \cdot AlSi_3O_{40}(F, OH)_8$; ideal formula C, $K_4 \cdot Li_7Al_6 \cdot Al_2Si_{14}O_{40}(F, OH)_8$; ideal formula D, $K_4 \cdot Li_5Al_6 \cdot Al_3Si_{13}O_{40}(OH, F)_8$; and ideal formula E, $K_4 \cdot Li_6Al_6 \cdot Al_4Si_{14}O_{40}(OH, F)_8$. The analyses may be divided into the types, A, B, C, D, and E with limits of composition expressed by the corresponding ideal formulas. One of the samples analyzed is close to polyolithionite (type A) in composition; eight samples are of type C, and five of the samples are of type D. Three samples do not correspond to any of the above types because of their bivalent ion content.

THE MICA STRUCTURE

The modern concept of the mica structure began with Mauguin's¹ measurements of the dimensions of mica unit cells with x -rays. Knowing the composition and density of a mica and the weights of the atoms, he was able to calculate the number of atoms of each element in the unit cell. Mauguin found that the number of atoms of oxygen plus fluorine in the mica unit cell is forty-eight, within the errors of analysis, and upon this value of the anion content of the unit cell are based modern mica formulas.

The concept of the mica structure is due to Pauling,² who showed that micas contain SiO_4 groups in sheets of indefinite extent. In these groups silicon has a coordination number of four, i.e., each silicon atom is surrounded by four oxygen atoms at the corners of a tetrahedron and the group is therefore referred to as the tetrahedral group. The silicon-oxygen sheet has the composition Si_4O_{10} , silicon atoms being linked through oxygen to form a hexagonal network. In the common micas a fourth of the silicon is replaced by aluminum so that the silicon-oxygen sheet has the composition $AlSi_3O_{10}$.

Two tetrahedral silicon sheets are held together firmly by cations in six-fold coordination, each cation being surrounded by six anions at the corners of an octahedron. Such a group is called an octahedral group. The octahedral groups may be built around aluminum, magnesium, titanium, manganese, iron, and lithium. Thus two silicon layers are joined through octahedral groups to form a double silicon layer. Many of the oxygen atoms are included in two groups.

These double silicon layers in turn are joined to other similar layers by large cations in twelve-fold coordination, consisting of potassium,

¹ Mauguin, C., Orientation of liquid crystals by mica sheets: *Compt. Rend.*, vol. 156, p. 1246, 1913. Also *Compt. Rend.*, vol. 186, pp. 879, 1131, 1928.

² Pauling, Linus, Structure of the micas and related minerals: *Nat. Acad. Sci. Proc.*, vol. 16, p. 123, 1930.

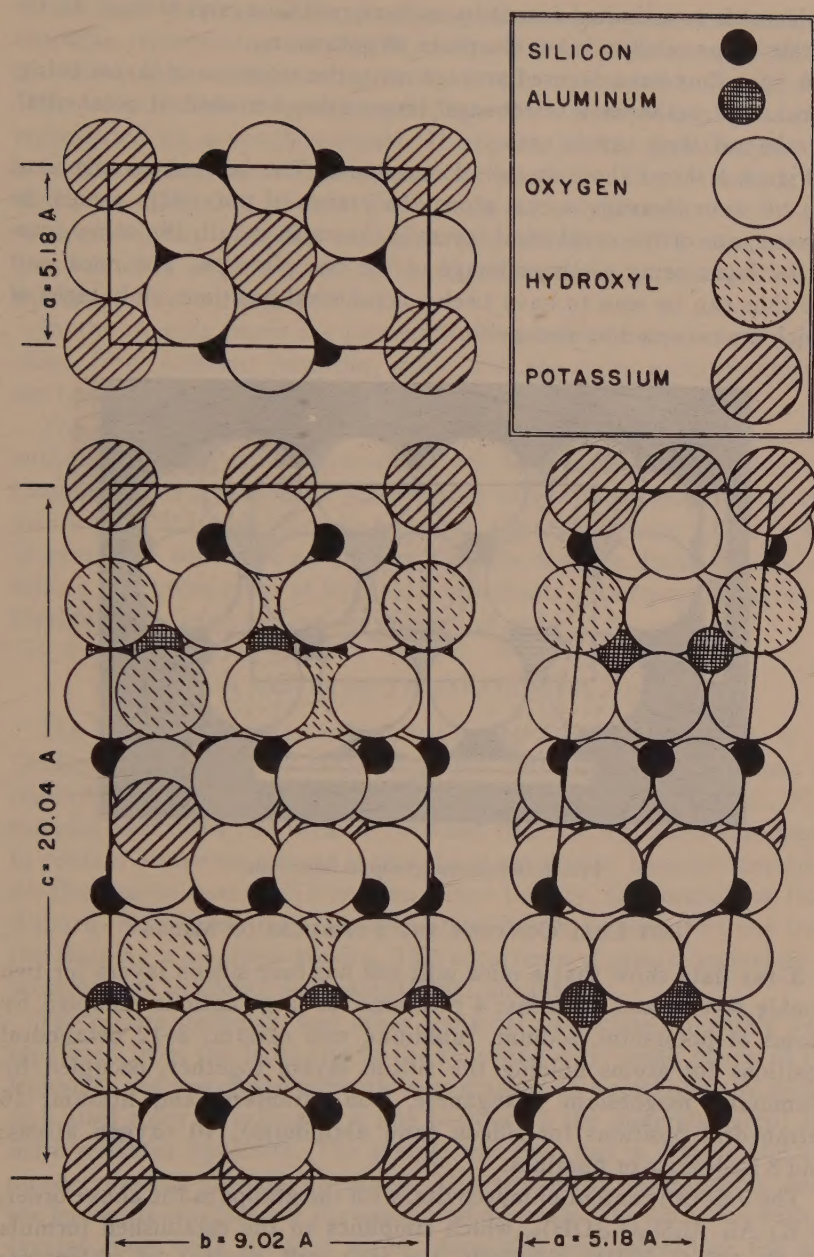


FIG. 1. Unit cell of muscovite.

replaceable to a limited extent by sodium, rubidium, and cesium. In the brittle micas calcium takes the place of potassium.

A mica thus has a layered arrangement, the sequence of layers being: tetrahedral, octahedral, tetrahedral, large cation, tetrahedral, octahedral, tetrahedral, large cation, etc.

Figure 1 shows the unit cell of muscovite. The layered arrangement can be seen; cleavage occurs along the planes of potassium atoms. In figure 2, one of the octahedral layers is shown in detail, the other octahedral layer being a mirror image of the one pictured. The mica unit cell thus can be seen to have twelve octahedral positions, only eight of which are occupied in muscovite.

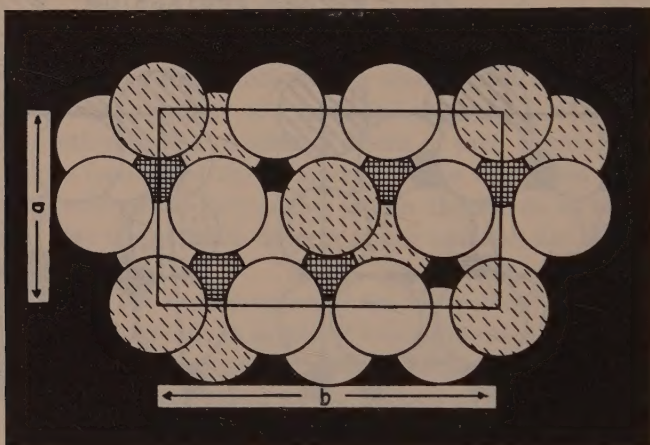


FIG. 2. Octahedral group in muscovite.

UNIT CELL CONTENT AND FORMULAS OF MICAS

X-ray data show that a mica unit cell has four silicon layers (or two double layers) and contains: 4 positions for large cations occupied by atoms of potassium, sodium, rubidium, and cesium; 8-12 octahedral positions for atoms holding the silicon layers together, occupied by aluminum, magnesium, manganese, iron, titanium, and lithium; 16 tetrahedral positions for silicon (and aluminum); 40 oxygen atoms; and 8 hydroxyls or fluorines.

The unit cell content of muscovite, with the groups in the above order, is $K_4 \cdot Al_8 \cdot Al_4Si_{12}O_{40}(OH)_8$, which simplifies to the established formula $K \cdot Al_2 \cdot AlSi_3O_{10}(OH)_2$. Similarly the unit cell content of phlogopite is $K_4 \cdot Mg_{12} \cdot Al_4Si_{12}O_{40}(F, OH)_8$, and the formula simplifies to $K \cdot Mg_3 \cdot AlSi_3O_{10}(F, OH)_2$.

Although the composition of common micas is given approximately by formulas representing one-fourth of the unit cell, the composition of lepidolite, apparently, cannot be so simply represented. Bragg³ says "The constitution of lepidolite diverges even more widely from that represented by a simple formula. It appears highly probable that Li is in six-coordination in the second of the groups. The formula $K \cdot Li_2 Al(Si_4O_{10}) (OH, F)_2$ [this is the formula of polyolithionite. R.E.S.] is approached, but it implies too high a lithium content. We must assume a substitution of part of the Si by Al, balanced by a reduction of the lithium in six-coordination."

In the present paper are presented seventeen new analyses of lepidolites, from different localities, made with the more recent analytical methods.

The interpretation of these analyses is based on the mica structure outlined above. Two interpretations will be presented: in the first, the composition is regarded as representing isomorphous mixtures of end members with simple mica formulas; in the second, some evidence will be presented which seems to show that the series is discontinuous, resulting in several types of lepidolite with limits of composition given in ideal formulas representing the entire unit cell.

SAMPLES AND THEIR PREPARATION FOR ANALYSIS

The lepidolite samples were furnished by Dr. Schaller, of the U. S. Geological Survey, who examined them optically to be sure that no impurities were present which could not be readily removed. Five samples were discarded because the small flakes of lepidolite were found to contain numerous minute inclusions of muscovite. Samples discarded for this reason were: two from San Diego County, California; one from Auburn, Maine; one from Tin Mountain, South Dakota; and one from the Harding mine, New Mexico. This occurrence of minute inclusions of muscovite in lepidolite is apparently not unusual.

The quartz, feldspar, and other commonly associated minerals were separated from the lepidolite in the following way: small pieces of the lepidolite and associated minerals were crushed on a steel plate by means of a steel roller, crushing to a fine powder all the minerals except the more resistant lepidolite. The sample was then put in a sieve and the powder passing through discarded. This treatment was repeated until the lepidolite was freed of the associated minerals. The mica was washed several times with distilled water, decanting and discarding the fine

³ Bragg, W. L., *Atomic Structure of Minerals*, p. 125, Cornell University Press, Ithaca, N. Y., 1937.

material that did not immediately settle to the bottom. The lepidolite was then examined optically by Dr. Schaller and when any impurities were found the treatment was repeated. The samples were then ground to pass an 80 mesh sieve.

The lepidolites analyzed, in order of increasing content of lithia, were as follows:

1. Large spherulitic plates, gray purple, Manitoba, Canada, U.S.N. Mus. 97635.
2. Coarse-medium grained, purple, Katerina mine, Pala, San Diego County, Calif.
3. Fine, compact, purple, Stewart mine, "40 acres," Pala, Calif.
4. Medium grained, purple, Panama-Pacific-Exposition mine, Chihuahua Valley, east of Oak Grove, San Diego County, Calif.
5. Medium grained, pink, west lens, Stewart mine, Pala, Calif.
6. Coarse, pale blue, silky or talc-like, Stewart mine, Pala, Calif.
7. Large plates, pale purple, Ohio City, Colo., U.S.N. Mus. 97893.
8. Coarse, purple, iron stained, Himalaya mine, Mesa Grande, San Diego County, Calif.
9. Coarse, purple, San Diego mine, Mesa Grande, Calif.
10. Large plates, gray purple, Wakefield, Canada, U.S.N. Mus. 96012.
11. Fine, almost white, Stewart mine, Pala, Calif.
12. Coarse, pale blue, Stewart mine, Pala, Calif.
13. Very coarse, purple, Himalaya mine, Mesa Grande, Calif.
14. Large transparent sheets, pale lavender, optically uniaxial, Calgoorie, W. Australia, U.S.N. Mus. R-4365.
15. Terminated crystals, pink, Little Three mine, Ramona, San Diego County, Calif., U.S.N. Mus. 93924.
16. Large plates, pale blue, Antsongombato, Madagascar, collected by Lacroix.
17. Polyolithionite, large plates, greenish, Greenland, U.S.N. Mus. 94314.

In addition, the alkalis alone were determined on a sample of purple muscovite from the Harding mine, New Mexico, described by Schaller and Henderson.⁴ The percentages of alkalis found were: Li_2O 0.38; Na_2O 0.91; K_2O 10.07; Rb_2O 0.82; Cs_2O 0.09.

METHODS OF ANALYSIS

A number of methods not commonly used in rock analysis had to be employed in analyzing the lepidolites. Rubidium was found in all of the samples and cesium in all but one; their determination was made by methods described by Wells and Stevens.⁵ Lithium was determined by the Palkin⁶ method.

Silica and fluorine were separated by the Berzelius method as modified

⁴ Schaller, W. T., and Henderson, E. P., Purple muscovite from New Mexico: *Am. Mineral.*, vol. 11, pp. 5-16, 1926.

⁵ Wells, R. C., and Stevens, R. E., Determination of the common and rare alkalis in mineral analysis: *Ind. Eng. Chem., Anal. Ed.*, vol. 6, pp. 439-442, 1934.

⁶ Palkin, S., Separation of lithium from the other alkali metals: *Am. Chem. Soc. Jour.*, vol. 38, p. 2326, 1916.

by Hoffman and Lundell,⁷ except that neutralization was made with hydrochloric acid instead of nitric. The silica was then obtained by acid dehydration in the usual way. Fluorine was determined nephelometrically.⁸

The determination of silica in polyolithionite (sample 17) gave with the silica a residue, non-volatile with HF, of nearly 12 milligrams from a half gram sample, as if decomposition of the mineral had not been complete. However, a second determination yielded an equally high residue and the figures for fluorine and silica checked well with the previous results (the figures for fluorine were 7.76% and 7.69%, for silica 59.52% and 59.59%). The residues were then examined spectrographically by George Steiger, of the Geological Survey, and found to consist essentially of columbium oxide. The columbium oxide was determined on a separate sample by fusion with sodium carbonate, evaporating to dryness with hydrochloric acid, filtering, and igniting the separated silica and columbium oxide. The silica was then removed with hydrofluoric acid. The columbium oxide was further purified by fusion with sodium carbonate, leaching the cake with water, adding to the extract hydrochloric acid to 5% strength, and digesting on the steambath to coagulate the columbium oxide and to dissolve the aluminum hydroxide. The columbium oxide was then filtered, ignited, and weighed. It was examined spectrographically by Mr. Steiger and found to be free of tantalum, which commonly accompanies columbium in other minerals.

In most of the lepidolites iron was present in such small quantity as to make its determination by reduction and titration with permanganate solution impracticable, and on all samples except 1, 10 and 17 the iron was determined by the thiocyanate colorimetric method. In the samples containing an appreciable quantity of iron it was found for the most part to be in the ferrous condition, so where total iron only was determined it is reported as ferrous oxide.

Manganese was determined colorimetrically after oxidation to permanganate. The manganese was found not to oxidize ferrous sulphate solutions; therefore most of it is present in the bivalent state and is reported as MnO.

For the determination of total water a half gram of the mineral was mixed with 1.5 grams of sodium tungstate and the water determined by the Penfield glass tube method. The mineral and flux were heated strongly with two blast lamps directed at opposite sides of the tube. An

⁷ Hoffman, J. I., and Lundell, G. E. F., Determination of fluorine and of silica in glasses and enamels containing fluorine: *Bur. Standards Jour. Research*, vol. 3, p. 581, 1929.

⁸ Stevens, R. E., Nephelometric determination of fluorine: *Ind. Eng. Chem., Anal. Ed.*, vol. 8, p. 248, 1936.

asbestos shield was used to prevent heating of the condensor end of the tube, which was covered with wet paper. By turning the tube over and over collapse of the glass tube was prevented until the charge had been heated sufficiently long for the volatilization of all water.

ANALYTICAL RESULTS

In Table 1 the results of the analyses are listed from left to right in order of increasing content of lithia. Table 3 gives corresponding relative equivalents and Table 4 atomic ratios. A gradation from a composition approaching that of muscovite (No. 1) to that of polyolithionite (No. 17) is indicated.

An increase in lithia content generally accompanies an increase in silica and a decrease in alumina, but there are some exceptions (note samples 6, 8, 13, 14), and other factors must be considered in explaining the composition of all lepidolites. In other words, lepidolites are not simply a solid solution of muscovite, or a hypothetical fluorine muscovite, with polyolithionite. With increase in lithia the fluorine usually increases, and with increase in fluorine the combined water decreases. The uncombined water (H_2O-) is taken as that given off below $110^{\circ}C.$, but the removal of all uncombined water at that temperature is doubtful. If the total loss in weight up to $160^{\circ}C.$ is taken as uncombined water, the combined water and fluorine approach closer the requirements of a mica.

Titanium and columbium were found to be constituents of those lepidolites which approach polyolithionite in composition (No. 17 from Greenland and No. 16 from Madagascar). As the micas had been found to be pure by optical examination the columbium is apparently a constituent of the mica.

Rubidium oxide was present in all samples, reaching a maximum of 2 per cent in sample 13 from Mesa Grande, California. Cesium oxide in smaller quantity, usually less than 0.5 per cent, was found in all the lepidolites except the polyolithionite from Greenland. These figures indicate that these rare alkalies are normal constituents of lepidolites, and the figures for K_2O given in most previous analyses may be too high.

In none of the lepidolites was more than a trace of calcium found. Calcium was precipitated as the oxalate and the precipitate would include any strontium in the mica.

Hahn, Strassmann, and Walling⁹ report the finding of strontium 87, radioactive disintegration product of rubidium, in a lepidolite from Manitoba, Canada. They found 2-3 per cent of rubidium and .0148 per

⁹ Hahn, Otto, Strassmann, Fritz, and Walling, Ernst, Herstellung wägbarer Mengen Strontiumisotops 87 als Umwandlungsprodukt des Rubidiums aus einem kanadischen Glimmer: *Naturwissenschaften*, vol. 25, p. 189, 1937.

TABLE 1

Sample No.	1	2	3	4	5	6	7	8	9
SiO ₂	47.00	49.50	48.58	50.20	49.29	53.45	49.58	54.69	51.70
Al ₂ O ₃	30.60	28.06	28.93	28.18	28.40	22.15	23.87	22.83	23.97
Cb ₂ O ₅	—	—	—	—	—	—	—	—	—
TiO ₂	Trace	Trace	Trace	Trace	Trace	Trace	.06	Trace	Trace
Fe ₂ O ₃	.26	—	—	—	—	—	—	—	—
FeO	.41	.11 ^a	.04 ^a	.04 ^a	.05 ^a	.16 ^a	.21 ^a	.11 ^a	.04 ^a
MgO	.13	None	None	None	.12	.14	None	None	None
MnO	2.04	.54	.92	.28	.65	.52	2.78	.14	.17
Li ₂ O	2.70	3.51	3.70 ^b	3.81	3.96	5.04	5.05	5.11	5.33
CaO	Trace	None	Trace	Trace	Trace	None	None	None	Trace
Na ₂ O	.77	1.27	.87	.64	.77	.74	.57	.57	.89
K ₂ O	9.52	10.32	10.02	9.91	9.93	9.58	10.14	9.53	10.79
Rb ₂ O	1.93	1.11	.91	1.55	1.56	1.56	1.62	1.64	.42
Cs ₂ O	.18	.13	.16	.11	.12	.48	.09	.17	.41
H ₂ O—	.25	.27	.54	.18	.14	.46	.51	.31	.26
H ₂ O+	2.18	2.15	2.56	2.18	1.76	1.28	1.22	1.02	1.24
F	4.09	5.98	4.93	4.97	6.52	7.22	7.49	6.86	7.76
O = F	102.06 1.72	102.95 2.52	102.16 2.08	102.05 2.09	103.27 2.75	102.78 3.04	103.19 3.15	102.98 2.89	102.98 3.27
H ₂ O 160°C.	100.34 .35	100.43 .38	100.08 .73	99.96 .27	100.52 .22	99.74 .65	100.04 .81	100.09 .50	99.71 .37

Sample No.	10*	11	12	13	14*	15	16	17
SiO ₂	50.31	51.10	52.58	51.25	51.07	54.40	57.03	59.56
Al ₂ O ₃	19.95	23.98	22.82	23.71	22.05	17.95	15.55	12.04
Cb ₂ O ₅	—	—	—	—	—	—	.14	1.52
TiO ₂	.22	Trace	Trace	.01	.06	.02	.03	.48
Fe ₂ O ₃	.49	—	—	—	—	—	—	.13
FeO	2.55	Trace	.01 ^a	.07 ^a	.23 ^a	.21 ^a	.12 ^a	.42
MgO	.02	None	None	.08	.09	.30	.22	.34
MnO	2.63	.13	.28	.61	.76	2.06	.72	.03
Li ₂ O	5.39	5.51	5.64	5.78	5.89	6.18	6.84	7.26
CaO	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Na ₂ O	.59	.63	.59	.65	.82	.72	.44	.53
K ₂ O	10.14	10.25	10.11	9.90	9.70	10.28	10.65	11.05
Rb ₂ O	.97	1.38	1.04	2.00	1.38	1.22	1.35	1.14
Cs ₂ O	.06	.48	.67	.08	.09	.24	.40	None
H ₂ O—	.66	.56	.30	.34	.96	.81	.74	.73
H ₂ O+	.88	1.50	1.35	.90	—	.58	.49	.47
F	7.65	7.36	7.56	8.08	7.13	9.19	9.00	7.73
O = F	102.51 3.22	102.88 3.10	102.95 3.18	103.46 3.40	100.23 3.00	104.16 3.87	103.72 3.79	103.43 3.26
H ₂ O 106°C.	99.29 .98	99.78 .88	99.77 .46	100.06 .45	97.23 1.74	100.29 1.18	99.93 .93	100.17 .76

* Total iron reported as FeO.

^b Results of other analysts suggest that this figure may be too high.

* Contaminated by organic matter during grinding.

cent of strontium. The age of this mineral is supposed to be about 2,000 million years. Most of the lepidolites in the present paper are probably a good deal younger and would contain less of strontium 87. Such small quantities of strontium could not be accurately determined without the use of very large samples.

EQUIVALENTS AND ATOMS IN THE MICA UNIT CELL

The structure of mica calls for the following requirements:

1. *Number of atoms in the unit cell:* (a) 40 oxygen atoms; (b) 8 positions for fluorine and hydroxyl; (c) 4 positions for potassium atoms (including sodium, rubidium, and cesium); (d) 8–12 octahedral positions for atoms of aluminum, iron, magnesium, manganese, titanium, and lithium; (e) 16 tetrahedral positions for silicon and aluminum.

The total number of atoms in the unit cell, therefore, varies from 76 to 80, counting the hydroxyl radical (OH) as one atom for simplicity. As the number of atoms in a unit cell is variable the total atoms cannot be used as a basis for calculating formulas. The number of tetrahedral cations (Si and Al) in the unit cell is fixed at 16.¹⁰

2. *Number of equivalents in the unit cell:* The unit cell must be neutral. This means that anion equivalents (the atomic weight divided by the valence of the atom) must be balanced by an equal number of cation equivalents. Anion equivalents in a unit cell of a mica are 88 (40 bivalent oxygen atoms and 8 univalent fluorines or hydroxyls). In the unit cell of muscovite $K_4 \cdot Al_3 \cdot Al_4Si_{12}O_{40}(OH, F)_8$, the 88 anion equivalents are balanced by 4 equivalents of potassium, 36 equivalents of aluminum, and 48 equivalents of silicon, making a total of 88 cation equivalents. Presumably the number of cation equivalents in a mica unit cell is an invariable quantity, always 88.

As the large cation in mica is filled by 4 equivalents of potassium there remain 84 equivalents to be distributed between the octahedral and tetrahedral groups. In the common micas which contain tetrahedral $Al_4Si_{12}O_{40}$, the tetrahedral group comprises 60 equivalents, leaving 24 equivalents for the octahedral group. In taeniolite,¹¹ however, and in polyolithionite, whose formula is derived in the section to follow, all 16 tetrahedral positions are filled by silicon, so that the tetrahedral group contains 64 equivalents which leaves only 20 equivalents for the octahedral group.

¹⁰ Bragg uses 4 tetrahedral atoms in $\frac{1}{2}$ unit cell. See Bragg, W. L., *Atomic Structure of Minerals*, p. 215, Cornell University Press, Ithaca, N. Y., 1937.

¹¹ Miser, H. D., and Stevens, R. E., Taeniolite from Magnet Cove, Arkansas: *Am. Mineral.*, vol. 23, p. 104, 1938.

Relative Equivalents in Lepidolites

The assignment of 84 equivalents to be distributed between the tetrahedral and octahedral groups is used in this paper as the basis for calculating the formulas and for comparing the compositions of the lepidolites.

TABLE 2. RELATIVE EQUIVALENTS (octahedral+tetrahedral=84)

	Eq. Wt.	1	2	3	4	5	6	7	8
octahedral and tetrahedral	SiO ₂	15.08	50.57	53.20	52.10	53.27	52.53	57.18	57.30
	Al ₂ O ₃	17.03	29.12	26.70	27.46	26.50	26.79	20.97	23.01
	Cb ₂ O ₅	26.58	—	—	—	—	—	—	—
	TiO ₂	19.98	—	—	—	—	—	.05	—
	Fe ₂ O ₃	26.61	.16	—	—	—	—	—	—
	FeO	35.92	.18	.05	.02	.03	.06	.10	.05
	MgO	20.16	.10	—	—	.10	.11	—	—
	MnO	35.45	.94	.24	.42	.13	.29	.24	1.28
	Li ₂ O	14.95	2.93	3.81	4.00	4.08	4.26	5.44	5.40
large cation			84.00	84.00	84.00	84.00	84.00	84.00	84.00
	Na ₂ O	31.00	.41	.66	.45	.34	.40	.39	.30
	K ₂ O	47.10	3.27	3.55	3.45	3.36	3.39	3.29	3.53
	Rb ₂ O	93.48	.34	.19	.16	.27	.27	.27	.28
	Cs ₂ O	140.86	.02	.02	.02	.02	.05	.02	.02
F+OH			4.04	4.42	4.08	3.99	4.08	4.00	4.13
	H ₂ O+	9.00	3.92	3.87	4.61	3.87	3.15	2.29	2.24
	F	19.00	3.48	5.11	4.19	4.19	5.51	6.13	6.48
			7.40	8.98	8.80	8.06	8.66	8.42	8.72

	9	10	11	12	13	14	15	16	17
octahedral and tetrahedral	SiO ₂	55.41	55.58	55.08	56.18	54.88	55.68	58.78	61.18
	Al ₂ O ₃	22.72	19.50	22.88	21.61	22.50	21.28	17.18	14.76
	Cb ₂ O ₅	—	—	—	—	—	—	—	.08
	TiO ₂	—	.18	—	—	.02	.05	.02	.03
	Fe ₂ O ₃	—	.30	—	—	—	—	—	.08
	FeO	.02	1.18	—	—	.03	.10	.10	.05
	MgO	—	.02	—	—	.06	.07	.24	.18
	MnO	.08	1.23	.06	.13	.27	.34	.95	.32
	Li ₂ O	5.77	6.01	5.98	6.08	6.24	6.48	6.73	7.40
large cation		84.00	84.00	84.00	84.00	84.00	84.00	84.00	84.00
	Na ₂ O	.47	.32	.33	.31	.34	.44	.37	.23
	K ₂ O	3.70	3.58	3.54	3.47	3.39	3.39	3.55	3.66
	Rb ₂ O	.08	.17	.24	.18	.34	.25	.21	.23
	Cs ₂ O	.05	.01	.05	.08	.02	.02	.03	.05
F+OH		4.30	4.08	4.16	4.04	4.09	4.10	4.16	4.17
	H ₂ O+	2.23	1.63	2.71	2.42	1.61		1.04	.87
	F	6.60	6.71	6.29	6.42	6.86		7.87	7.67
		8.83	8.34	9.00	8.84	8.47		8.91	8.54

TABLE 3. ATOMIC RATIOS IN LEPIDOLITES

		1	2	3	4	5	6	7	8	9
	tetrahedral	Si	12.64	13.30	13.03	13.32	13.13	14.30	13.51	14.33
		Al	3.36	2.70	2.97	2.68	2.87	1.70	2.49	1.67
	tetrahedral		16.00	16.00	16.00	16.00	16.00	16.00	16.00	16.00
	octahedral	Al	6.35	6.20	6.18	6.15	6.06	5.29	5.19	5.42
		Cb	—	—	—	—	—	—	—	—
		Ti	—	—	—	—	—	.01	—	—
		Fe ⁺⁺⁺	.05	—	—	—	—	—	—	—
		Fe ⁺⁺	.09	.03	.01	.01	.02	.03	.05	.03
		Mg	.05	—	—	—	.05	.06	—	—
		Mn	.47	.12	.21	.07	.15	.12	.64	.03
		Li	2.93	3.81	4.00	4.08	4.26	5.44	5.56	5.40
	large cation		9.94	10.16	10.40	10.31	10.54	10.94	11.45	10.85
		Na	.41	.66	.45	.34	.40	.39	.30	.28
	large cation	K	3.27	3.55	3.45	3.36	3.39	3.29	3.53	3.19
		Rb	.34	.19	.16	.27	.27	.27	.28	.29
		Cs	.02	.02	.02	.02	.02	.05	.02	.02
			4.04	4.42	4.08	3.99	4.08	4.00	4.13	3.78
	large cation	H	3.92	3.87	4.61	3.87	3.15	2.29	2.24	1.79
	large cation	F	3.48	5.11	4.19	4.19	5.51	6.13	6.48	5.70
		O	44.24	43.59	44.25	43.84	42.86	42.08	41.95	41.94
	large cation	O+F	47.72	48.70	48.44	48.03	48.37	48.21	48.43	47.64
	large cation		48.57							

		10	11	12	13	14	15	16	17
	tetrahedral	Si	13.90	13.77	14.05	13.72	13.92	14.70	15.30
		Al	2.10	2.23	1.95	2.28	2.08	1.30	.70
	tetrahedral		16.00	16.00	16.00	16.00	16.00	16.00	16.00
	octahedral	Al	4.40	5.40	5.25	5.22	5.01	4.43	4.22
		Cb	—	—	—	—	—	—	.02
		Ti	.04	—	—	—	.01	—	.01
		Fe ⁺⁺⁺	.10	—	—	—	—	—	—
		Fe ⁺⁺	.59	—	—	.02	.05	.05	.02
		Mg	.01	—	—	.03	.04	.12	.09
		Mn	.62	.03	.07	.14	.17	.48	.16
		Li	6.01	5.98	6.08	6.24	6.48	6.73	7.40
	large cation		11.77	11.41	11.40	11.65	11.76	11.81	11.92
		Na	.32	.33	.31	.34	.44	.37	.23
	large cation	K	3.58	3.54	3.47	3.39	3.39	3.55	3.66
		Rb	.17	.24	.18	.34	.25	.21	.23
		Cs	.01	.05	.08	.02	.02	.03	.05
			4.08	4.16	4.04	4.09	4.10	4.16	4.17
	large cation	H	1.63	2.71	2.42	1.61		1.04	.87
	large cation	F	6.71	6.29	6.42	6.86		7.87	7.67
		O	41.50	42.29	42.02	41.42		40.67	40.69
	large cation	O+F	48.21	48.58	48.44	48.28		48.54	48.36
	large cation								47.78

In Table 2 the relative equivalents are given, on the basis of 84 tetrahedral and octahedral equivalents, and in Table 3 the corresponding *atomic ratios* are listed. Correlation of the analyses on this basis allows a precise evaluation of octahedral groups, on which the interpretation largely depends. Satisfactory agreement with the mica requirements may be seen in Tables 2 and 3.

FORMULA OF POLYLITHIONITE

Polyolithionite was first described by Lorenzen,¹² whose analysis gives the alkali content as follows: Li_2O 9.04, Na_2O 7.63, and K_2O 5.37 per cent. So far as is known sample 17 in this paper is the same as Lorenzen's sample. Flink¹³ described a mica from Narsarsuk, Greenland, similar to polyolithionite, and his figures for alkalies are Li_2O 8.24, Na_2O 1.61, K_2O 11.05 per cent. Neither of these analyses list rubidium, cesium, or columbium.

Detailed study of the mica unit cell shows that there are only twelve octahedral positions (Fig. 2), and apparently lithium occupies octahedral positions in the mica. Sufficient octahedral positions are not available to account for the high lithium content reported for polyolithionite by Lorenzen and by Flink. Lorenzen's figures for Na_2O and K_2O also seem questionable. These two analyses do not give the same formula for polyolithionite as that derived from sample 17 in the present paper.

The scheme described in the previous section was used in calculating the formula of polyolithionite from the analysis of sample 17. This calculation is shown in Table 4. The inclusion of columbium in the octahedral group is logical though not as yet confirmed by x-ray data.

The unit cell content is closely represented by $\text{K}_4 \cdot \text{Li}_3\text{Al}_4 \cdot \text{Si}_{16}\text{O}_{40}\text{F}_8$, and the formula simplifies to $\text{K} \cdot \text{Li}_2\text{Al} \cdot \text{Si}_4\text{O}_{10}\text{F}_2$. The analysis shows minor substitution of aluminum for silicon and of columbium, titanium, iron, magnesium and manganese for octahedral aluminum and lithium. A slight deficiency of fluorine and hydroxyl for the required F_8 may indicate a substitution of oxygen in this anion group.

A brief study of mica unit cells will suffice to show that polyolithionite has the maximum ratio of lithium in a mica, as the octahedral group is limited to 12 atoms and valency must be balanced, unless it is possible to substitute lithium in another group. For a pure completely fluorinated polyolithionite the percentage of Li_2O is 7.65 and with substitution of hydroxyl for fluorine a slightly higher figure (7.73%) may be obtained.

¹² Lorenzen's analyses are given under zinnwaldite on p. 627 of Dana's System of Mineralogy.

¹³ Flink, Gustav, On the minerals from Narsarsuk on the Firth of Tunugdliarfik in southern Greenland: *Meddelelser om Grönland*, vol. 24, pp. 110-115, 1901.

TABLE 4. CALCULATION OF FORMULA OF POLYLITHIONITE

	Per cent	Eq. Wt.	Equivalent Ratios		Atomic Ratios	
SiO ₂	59.56	15.08	3.949	63.12	15.78	Si ₁₆
Al ₂ O ₃	12.04	17.03	.706	11.27	3.76	Al ₄
Cb ₂ O ₅	1.52	26.58	.057	.91		
TiO ₂	.48	19.98	.024	.38		
Fe ₂ O ₃	.13	26.61	.005	.08		
FeO	.42	35.92	.012	.19		
MgO	.34	20.16	.017	.27		
MnO	.03	35.45	.001	.02		
Li ₂ O	7.26	14.95	.486	7.76	7.76	Li ₈
			5.257	84.00		
Na ₂ O	.53	31.00	.017	.27		
K ₂ O	11.03	47.10	.235	3.76		
Rb ₂ O	1.14	93.48	.012	.19		
			.264	4.22	4.22	K ₄
H ₂ O+	.47	9.00	.052	.83		
F	7.73	19.00	.407	6.51		
			.459	7.34	7.34	F ₃

Unit cell content: $K_4 \cdot Li_8 Al_4 \cdot Si_{16} O_{40} F_3$.Formula: $K \cdot Li_2 Al \cdot Si_4 O_{10} F_2$.

The high percentages of Li₂O reported by Lorenzen and by Flink do not seem to be theoretically possible.

INTERPRETATION OF THE LEPIDOLITES AS ISOMORPHOUS MIXTURES

The percentages found in the analyses in Table 1 are very close to those that would be obtained in an isomorphous mixture of four end member micas, namely: polyolithionite, $K \cdot Li_2 Al \cdot Si_4 O_{10} F_2$; biotite, $K \cdot (Mn, Fe, Mg)_3 \cdot AlSi_3 O_{10} (F, OH)_2$; lithium muscovite, $K_4 \cdot Li_6 Al_6 \cdot Al_4 Si_{12} O_{40} (F, OH)_8$; and muscovite, $K \cdot Al_2 \cdot AlSi_3 O_{10} (OH, F)_2$.

The formulation of polyolithionite in the previous section supplies one of the missing end members in the series. The formula for lithium muscovite, as far as the writer knows, is hypothetical and represents the maximum lithium that may substitute for aluminum in the muscovite formula. It must be included to account for the lithium content found in the lepidolites. The biotite formula is represented by the bivalent cations in the analysis and is usually that of a manganese biotite with substitution of iron and magnesium for manganese in some of the samples. The

biotite may be divided, if desired, into a manganese biotite, an iron biotite, and a magnesium biotite (phlogopite), but for simplicity they have been taken as one component in the calculations.

Method of Calculating Ratios of End Member Micas

The calculation of the unit cell formula ratios is simple and involves few assumptions so that they should be accurate. These formula ratios may be calculated either from the relative equivalents (Table 2), the atomic ratios (Table 3), or, with more difficulty, the writer thinks, from the percentages in Table 1. The equations used to calculate the formula ratios are as follows:

$$\text{Polyolithionite} = \frac{\text{SiO}_2 - 48}{16}$$

$$\text{Biotite} = \frac{R''}{24}$$

$$\text{Lithium muscovite} = \frac{\text{Li} - 8P}{6}, \text{ where SiO}_2, R'', \text{ and Li are given in rela-}$$

tive equivalents for 84 octahedral and tetrahedral equivalents, and P is the unit cell formula ratio of polyolithionite. The muscovite was found by difference.

These ratios are of the unit cell formulas so that all are comparable with the larger formula for lithium muscovite.

To calculate the weight percentages of the end members from the unit cell formula ratios a number of assumptions are involved. The unit cell formula ratios were divided by the respective unit cell weights in obtaining the weight percentages of end members. With which end member the hydroxyl, sodium, rubidium, and cesium should be counted could not be told, so the end members taken were the potassium and fluorine unit cells, thus distributing the hydroxyl, sodium, rubidium, and cesium equally. The biotite unit cell weight was calculated for each sample from the ratios of the bivalent ions present (manganese, iron, and magnesium).

The figures obtained in the above calculations were then adjusted to add to 100 per cent. No correction was made for uncombined water.

Table 5 gives the unit cell formula ratios and Table 6 the weight percentages of the end member micas found by calculation. In Table 7 the silica, alumina, and lithia are calculated from the weight percentages of the end members. A close agreement between the calculated values and those determined shows that the compositions may be given satisfactorily in terms of the four end members chosen. The determined values for sample No. 17 in Table 7 are lower than those calculated because of the heavy elements columbium and titanium present in the mineral.

TABLE 5. UNIT CELL FORMULA RATIOS OF END MEMBER MICAS IN LEPIDOLITES

Sample No.	Polyolithionite	Biotite	Lithium Muscovite	Muscovite
1	.1606	.0508	.2742	.5144
2	.3250	.0121	.2017	.4612
3	.2562	.0183	.3251	.4004
4	.3294	.0063	.2408	.4235
5	.2831	.0175	.3325	.3669
6	.5739	.0171	.1415	.2675
7	.3750	.0575	.4267	.1408
8	.5815	.0046	.1247	.2892
9	.4630	.0042	.3443	.1885
10	.4737	.1012	.3698	.0551
11	.4425	.0025	.4067	.1483
12	.5115	.0054	.3313	.1518
13	.4300	.0151	.4667	.0883
14	.4800	.0213	.4400	.0587
15	.6737	.0538	.2234	.0491
16	.8237	.0229	.1351	.0183
17	.9450	.0200	.0334	.0016

TABLE 6. WEIGHT PERCENTAGES OF END MEMBER MICAS IN LEPIDOLITES
(uncorrected for H₂O—)

Sample No.	Polyolithionite	Biotite	Lithium Muscovite	Muscovite
1	15.5	6.4	27.1	51.1
2	31.8	1.6	20.2	46.5
3	25.0	2.3	32.4	40.2
4	32.3	.8	24.1	42.8
5	27.7	2.2	33.2	36.9
6	56.6	2.1	14.3	27.1
7	36.3	7.3	42.3	14.1
8	58.2	.6	12.4	28.9
9	45.7	.5	34.7	19.1
10	45.5	12.8	36.3	5.4
11	43.6	.3	41.0	15.1
12	50.4	.7	33.4	15.4
13	42.3	1.9	46.9	8.9
14	47.2	2.7	44.2	5.9
15	66.0	6.7	22.4	5.0
16	81.6	2.8	13.7	1.9
17	94.2	2.4	3.4	.2

TABLE 7. COMPARISON OF CALCULATED AND DETERMINED VALUES FOR
 SiO_2 , Al_2O_3 , AND Li_2O
 (corrected for H_2O —, OH, Na, Rb, and Cs)

Sample No.	SiO_2		Al_2O_3		Li_2O	
	Calc.	Found	Calc.	Found	Calc.	Found
1	47.0	47.00	30.8	30.60	2.7	2.70
2	49.7	49.50	28.0	+ .26 Fe_2O_3 28.06	3.5	3.51
3	48.4	48.58	28.8	28.93	3.7	3.70
4	50.2	50.20	28.2	28.18	3.8	3.81
5	48.9	49.29	28.2	28.40	4.0	3.96
6	53.6	53.45	22.2	22.15	5.1	5.04
7	49.6	49.58	24.0	23.87	5.1	5.05
8	54.5	54.69	22.6	+ .06 TiO_2 22.83	5.1	5.11
9	52.2	51.70	24.2	23.97	5.4	5.33
10	50.2	50.31	20.4	19.95	5.4	5.39
11	51.3	51.10	24.1	+ .49 Fe_2O_3 + .22 TiO_2 23.98	5.5	5.51
12	52.8	52.58	22.8	22.82	5.7	5.64
13	51.2	51.25	23.8	23.71	5.8	5.78
14	51.8	51.07	22.4	22.05	6.0	5.89
15	54.4	54.40	18.0	17.95	6.2	6.18
16	57.2	57.03	15.75	15.55	6.9	6.84
17	60.5	59.56	13.7	12.04	7.4	7.26
				+1.52 Cb_2O_6 + .48 TiO_2		

The selection of end members is an arbitrary one. Other combinations of four end members which express the compositions equally well are: polyolithionite, zinnwaldite (assuming its formula to be $\text{K} \cdot \text{LiR}''\text{Al} \cdot \text{AlSi}_3\text{O}_{10}\text{F}_2$),¹⁴ lithium muscovite, and muscovite; polyolithionite, taeniolite ($\text{K} \cdot \text{LiR}''_2 \cdot \text{Si}_4\text{O}_{10}\text{F}_2$), lithium muscovite, and muscovite. In addition five or six of the above end members may be taken, depending on what end members are used to express the bivalent ion content. Selection of polyolithionite, biotite, lithium muscovite; and muscovite as end members serves to express the composition in the simplest way.

EVIDENCE OF DISCONTINUOUS ISOMORPHISM AND ITS INTERPRETATION

In crystalline substances there seems to be a tendency toward simple atomic ratios. This tendency is illustrated by the fact that in many solu-

¹⁴ Bragg gives $\text{K} \cdot \text{LiFeAl} \cdot (\text{Al} \cdot \text{Si}_3\text{O}_{10})(\text{OH}, \text{F})_2$. See Bragg, W. L., Atomic Structure of Minerals, p. 215, 1937.

tions of salts the individual salts crystallize separately, as solids having simple compositions.

If the lepidolite series is one of complete isomorphism of end members there would be no tendency to form simple ratios of atoms. In the process of their crystallization a surface of one composition would be covered by a layer of a different composition. For like to crystallize on like seems more plausible and this tendency would result in incomplete isomorphism. It seems well to examine the lepidolite analyses further to see if isomorphism is or is not continuous.

Simple Mica Unit Cells

A large number of mica unit cells having simple ratios of whole atoms are possible. Starting with muscovite with 12 atoms of silicon and 4 atoms of tetrahedral aluminum in a unit cell and replacing aluminum by silicon, atom for atom, the tetrahedral groups would be $\text{Al}_4\text{Si}_{12}\text{O}_{40}$, $\text{Al}_3\text{Si}_{13}\text{O}_{40}$, $\text{Al}_2\text{Si}_{14}\text{O}_{40}$, $\text{AlSi}_{15}\text{O}_{40}$, and $\text{Si}_{16}\text{O}_{40}$. As the tetrahedral and octahedral equivalents total 84, the equivalents in the octahedral group depend on which of the tetrahedral groups is present. With tetrahedral $\text{Al}_4\text{Si}_{12}\text{O}_{40}$ (60 equivalents) the octahedral equivalents would be 24; tetrahedral $\text{Al}_3\text{Si}_{13}\text{O}_{40}$ (61 equivalents) leaves 23 equivalents for the octahedral group; tetrahedral $\text{Al}_2\text{Si}_{14}\text{O}_{40}$ (62 equivalents) leaves 22 equivalents for the octahedral group; tetrahedral $\text{AlSi}_{15}\text{O}_{40}$ (63 equivalents) leaves 21 equivalents for the octahedral group; and tetrahedral $\text{Si}_{16}\text{O}_{40}$ leaves 20 equivalents for the octahedral group.

Then, starting with the octahedral groups filled with aluminum and replacing the aluminum atoms with other octahedral components, all combinations of whole atoms in unit cells may be devised.

The simple unit cell combinations are shown in figure 3 by the spaces containing the numbers. The numbers represent the octahedral aluminum atoms in the unit cell, corresponding octahedral equivalents other than aluminum are at the left, and the corresponding tetrahedral group is given below. Several unit cells may be represented by each square filled by a number, depending on what elements other than aluminum are in the octahedral group. Octahedral elements other than aluminum are in equivalents as these elements differ in valence.

The unit cells of muscovite (M), zinnwaldite (Z), biotite (B), taeniolite (T), and polyolithionite (P) are shown in figure 3. These so-called end member unit cells are non-polar, one side being a mirror image of the side opposite. Most of the intermediate unit cells are polar and for that reason would probably not have as great a tendency to repeat in a crystal as would the non-polar end member unit cells.

As a means of referring to the different unit cells in figure 3 the tetra-

hedral and octahedral constituents will be given in the following order: 1. octahedral *equivalents* other than aluminum; 2. octahedral aluminum *atoms*; 3 silicon *atoms*. The unit cell of muscovite, $K_4 \cdot Al_3 \cdot Al_4 Si_{12} O_{40} (OH)_8$ in the lower right corner in figure 3 is given by the symbols 0-8-12.

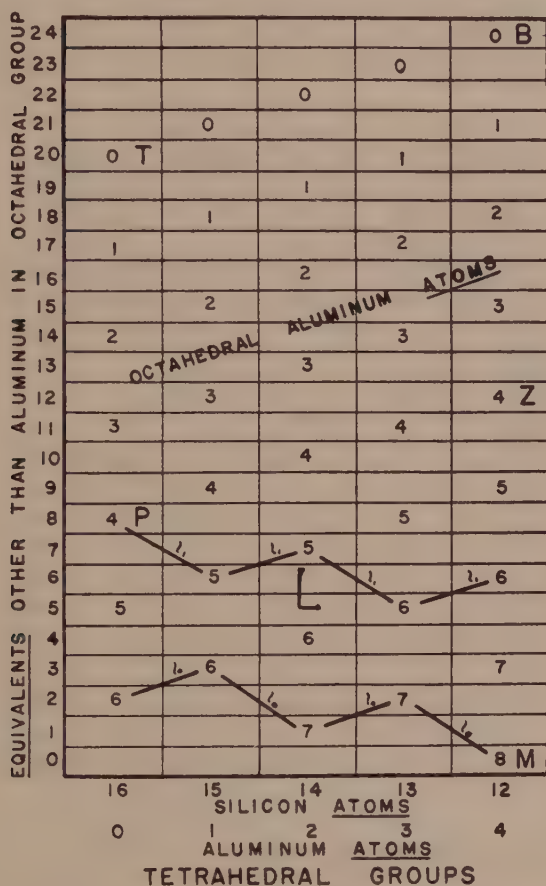


FIG. 3. Octahedral and tetrahedral groups in mica unit cells, ranging from tetrahedral $(AlSi_3O_{10})_4$ to $(Si_4O_{10})_4$. Numbers within the diagram represent octahedral aluminum atoms, the remaining octahedral equivalents being at the left, and corresponding tetrahedral groups at the bottom.

l_0 : Formulas below this line contain less than the minimum octahedral positions (8).

l_1 : Unit cells containing only lithium and aluminum in octahedral positions are below this line.

M=muscovite. Z=zinnwaldite. B=biotite.

T=taeniolite. P=polyolithionite.

L=probable lepidolite area.

Limits of Substitution in Lepidolites

Certain limits of substitution in figure 3 have theoretical significance. No unit cells are shown below the line marked l_0 because below that line the total number of octahedral positions occupied is less than 8, the minimum as far as is known. If the octahedral group consists only of lithium and aluminum the unit cell composition cannot be above l_1 , for above that line the octahedral atoms (Li+Al) would exceed 12, and there

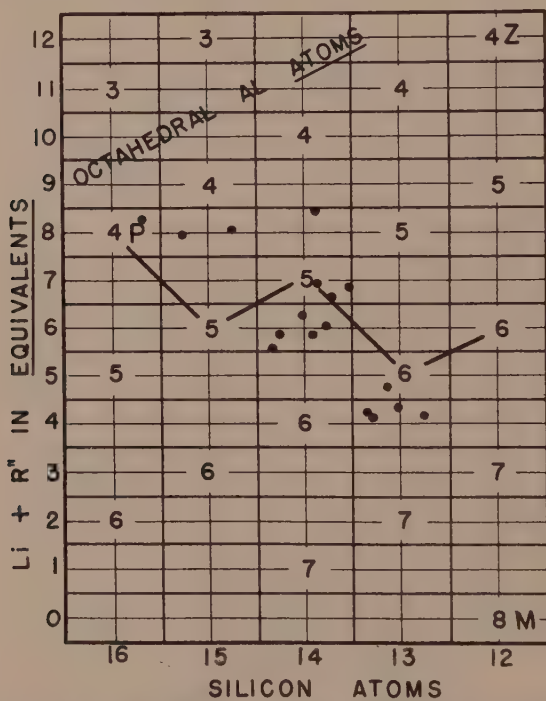


FIG. 4. Tetrahedral Si plotted against octahedral Li and R'' in lepidolites. Unit cells are designated by the numbers within the diagram as in figure 3.

are only 12 octahedral positions available in a mica unit cell. Therefore lepidolites containing no octahedral ions other than lithium and aluminum, as is essentially true of most of the lepidolites analyzed, would necessarily fall between the limits l_0 and l_1 , in figure 3. With a bivalent ion present in the octahedral group the unit cell composition may be above the limit l_1 , for one atom of a bivalent ion (such as Mn, Fe^{++} , and Mg) may take the place of two atoms of univalent lithium, ions in octahedral positions thus being reduced in numbers.

As the octahedral group in most of the lepidolites consists essentially of only lithium and aluminum, their compositions, for the most part, would lie under the limit l_1 , and somewhere between muscovite and polyolithionite, probably near the area marked with the large L in figure 3.

Figure 4 is a diagram consisting of the lower part of figure 3 and on which the silicon atoms per unit cell, calculated from the analyses, are plotted against the lithium and bivalent ion content in equivalents. The small quantities of other octahedral ions with valences greater than two are considered as substituting for aluminum.

As predicted in the discussion of figure 3 the compositions fall below the limit l_1 , except where bivalent ions cause them to go above that limit. A grouping of compositions may be seen in figure 4 immediately below the unit cells 7-5-14 and 5-6-13, which, together with polyolithionite, 8-4-16, the unit cell 6-5-15, and the unit cell 6-6-12, outline the limit l_1 . Theoretical considerations, therefore, indicate that the above unit cells represent ideal formulas, three of which are approximated by the analyses.

Ideal Formulas for Lepidolites

The ideal formulas, which are suggested by this discussion, are as follows:

Ideal formula A is polyolithionite, $K \cdot Li_2Al \cdot Si_4O_{10}F_2$, unit cell 8-4-16 in figures 3 and 4.

Ideal formula B, $K_4 \cdot Li_6Al_5 \cdot AlSi_{15}O_{40}(F, OH)_8$, unit cell 6-5-15 in figures 3 and 4.

Ideal formula C,¹⁵ $K_4 \cdot Li_7Al_5 \cdot Al_2Si_{14}O_{40}(F, OH)_8$, unit cell 7-5-14 in figures 3 and 4.

Ideal formula D, $K_4 \cdot Li_5Al_6 \cdot Al_3Si_{13}O_{40}(F, OH)_8$, unit cell 5-6-13 in figures 3 and 4.

Ideal formula E,¹⁵ $K_4 \cdot Li_6Al_6 \cdot Al_4Si_{12}O_{40}(F, OH)_8$, unit cell 6-6-12 in figures 3 and 4. This is the formula for lithium muscovite, proposed as an end member in the previous section.

Three points in figure 4, representing samples 10, 15, and 16, are well above the limit l_1 due to their content of bivalent ions. Samples well above the limit l_1 probably represent more nearly a condition of complete isomorphism as above that limit neighboring unit cells may be more nearly alike.

That the compositions approximate only roughly the ideal formulas is apparent, but nevertheless the lepidolites may be divided into groups

¹⁵ Niggli has proposed these two as ideal formulas for lepidolites, with Na replacing Li. See Niggli, Paul, Über die chemische Zusammensetzung der Alkaliglimmer: *Zeits. Kryst.*, vol. 96, p. 96, 1937.

whose limits of composition are given by the ideal formulas. These limits of composition may also be expressed in terms of end member micas. It seems apparent that in such a solid solution the end members would not be present as individual end member unit cells, but that the ions of which the end members are composed would be distributed uniformly throughout the structure. Such a uniform distribution of ions would involve the limits of composition expressed in the ideal formulas.

Types of Lepidolites

The lepidolites, therefore, may be divided into types as follows:

Type A. Limit of composition ideal formula A, polyolithionite, $K \cdot Li_2Al \cdot Si_4O_{10}F_2$. Presumably this formula has the maximum content of lithium in a mica. Sample 17 is essentially polyolithionite.

Type B. Limit of composition ideal formula B, $K_4 \cdot Li_6Al_5 \cdot AlSi_{15}O_{40} \cdot (F, OH)_8$, one formula of muscovite to three of polyolithionite. Further substitution of Li_3 for Al in the formula would require 13 octahedral positions and only 12 are contained in a mica unit cell. Substitution of $LiMn$ for Al is structurally possible (octahedral positions filled would then be 12) and this substitution seems to have occurred in samples 15 and 16.

Type C. Limit of composition ideal formula C, $K_4 \cdot Li_7Al_5 \cdot Al_2Si_{14}O_{40} \cdot (F, OH)_8$. This type has approximately one unit cell formula of polyolithionite to not more than one unit cell formula of lithium muscovite. Samples 6, 7, 8, 9, 11, 12, 13, and 14 have this composition, as shown in Table 5 and in figure 4.

Type D. Limit of composition ideal formula D, $K_4 \cdot Li_5Al_6 \cdot Al_3Si_{13}O_{40} \cdot (OH, F)_8$. This type has approximately one unit cell formula of polyolithionite to not more than two unit cell formulas of lithium muscovite and not less than one unit cell formula of muscovite. Samples 1, 2, 3, 4, and 5 have this composition, as shown in Table 5, and figure 4.

Type E. Limit of lithium content ideal formula E, $K_4 \cdot Li_6Al_6 \cdot Al_4Si_{12}O_{40}(OH, F)_8$, the formula of lithium muscovite. None of the samples is of this composition.

ACKNOWLEDGMENTS

The writer wishes to acknowledge the kindly cooperation of Dr. W. T. Schaller, who furnished the samples, verified their purity optically, and critically reviewed the paper. The interest of Dr. R. C. Wells, who reviewed the manuscript, and the help of Mr. George Steiger, who examined spectrographically the columbium oxide from polyolithionite, are gratefully acknowledged.

MODELS TO AID IN VISUALIZING THE OPTICAL PROPERTIES OF CRYSTALS

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INTRODUCTION

The study of crystal optics is largely a matter of solid geometry, and demands clear visualization of optical properties in their three-dimensional relations. To aid students in visualizing these relations, numerous models of wood, wire, glass, and plaster have been devised,¹ and have proven to be of definite value. The models described in this paper were designed, in part to supplement, and in part to substitute for standard types already in use. Following the precedent of Wright² and Rogers,³ emphasis is placed on the indicatrix, or index ellipsoid, and its relations to crystallographic directions and to common optical phenomena. Relations heretofore shown only by two-dimensional drawings, by solid opaque models, or by elusive wire "bird cages" are clearly represented in three dimensions by transparent models made of sheet celluloid.

The models described below were constructed for the Petrographic Laboratory of the University of Kansas by student workers as a project under the National Youth Administration. Particular credit is due to Mr. Hugh Magruder and to Mr. Raymond Leonard for skilled workmanship and for ingenuity in working out details of construction. Photographs of the models were made by Mr. Oren Bingham, director of the University Photographic Bureau.

MATERIALS, EQUIPMENT, AND METHODS

Sheet celluloid constitutes the basic material for the models. This material has the advantages of being easily tooled and cemented, and of being practically unbreakable. It may be purchased in thicknesses of .08 in. and .125 in., both sizes being used in the various models. Originals

¹ Wright, F. E., A device to aid in the explanation of interference phenomena: *Am. Jour. Sci.*, vol. 26, p. 536, 1908.

Johannsen, Albert, Manual of Petrographic Methods, McGraw-Hill, New York, 1914, Fig. 162.

Rosenbusch, H., and Wülfing, E. A., Mikroskopische Physiographie der Mineralien und Gesteine, Band I, Erste Hälfte, Stuttgart, 1924, Figs. 84, 90, and 94.

Rogers, A. F., A model for biaxial crystals: *Am. Mineral.*, vol. 19, pp. 206-208, 1934.

Catalogues of Dr. F. Krantz, Bonn, Germany.

² Wright, F. E., The index ellipsoid (optical indicatrix) in petrographic microscope work: *Am. Jour. Sci.*, vol. 35, pp. 133-138, 1913.

³ Rogers, A. F., Introduction to the Study of Minerals, McGraw-Hill, New York, 1937, pp. 176-181.

of the models described below were constructed of the highly inflammable nitrate celluloid, purchased from the Frederick Post Co., Box 803, Chicago, Illinois. Later it was learned that the relatively non-inflammable acetate celluloid might be purchased from the Plastics Department, E. I. Du Pont de Nemours & Co., Arlington, New Jersey, under the trade name "Plastacele." The latter is recommended.

Tools required for construction of the models are few and simple, and are listed below:

Jeweler's hand saw	Scale
Carpenter's square	Protractor
Carpenter's compass	Ellipsograph
Scriber	Woodworking lathe
Clamps	Medium sandpaper
Straightedge	

For the scribe, a heavy sewing needle or a victrola needle held in a pin vice may be used. The ellipsograph is easily made by cutting a narrow slot in a strip of brass or bakelite about 9 inches long and about .6 in. wide (Fig. 1). A slender, flat-headed pin (A) is fixed in position just beyond one end of the slot, and in line with its center. A second similar pin (B) is placed in the slot so as to slide freely to any given point and then be locked in position. Between these two pins, a scribing point (C) is inserted in the slot, so as to be adjustable to any position between A and B. In using the instrument, a steel square serves as a guide, as explained under Fig. 1.

Celluloid is tooled in much the same way as wood. Straight lines are laid out with straightedge, scale, protractor, and carpenter's square, and marked with a scribe. Curved lines are marked off with the carpenter's compass or ellipsograph, as the case may require. Parts are then cut out with a jeweler's hand saw, using a one-inch board with a deep V-shaped notch as a support for the celluloid. Sandpaper is used for smoothing sawed edges, and, if necessary, for reducing parts to correct dimensions. In carrying out these operations, particular care should be exercised to avoid scratching the celluloid, which is relatively soft and easily marred.

In cementing celluloid, the surfaces to be joined are first made to fit closely at all points. Each surface is then coated with a dilute solution of celluloid in acetone, a few moments allowed for partial drying, a second coat applied, and the parts then are pressed firmly together and held in position for a few minutes until initial set is acquired. Permanent set is attained in a few hours. If cementing is properly done, the joint, or "weld," will be fully as strong as other parts of the celluloid. In acquiring the technique of cementing, some experimentation with scrap material may be desirable. Proper viscosity of the cement is important: if too low,

the fluid is too mobile and difficult to control; if too high, the fluid is syrupy and makes an uneven, messy joint.

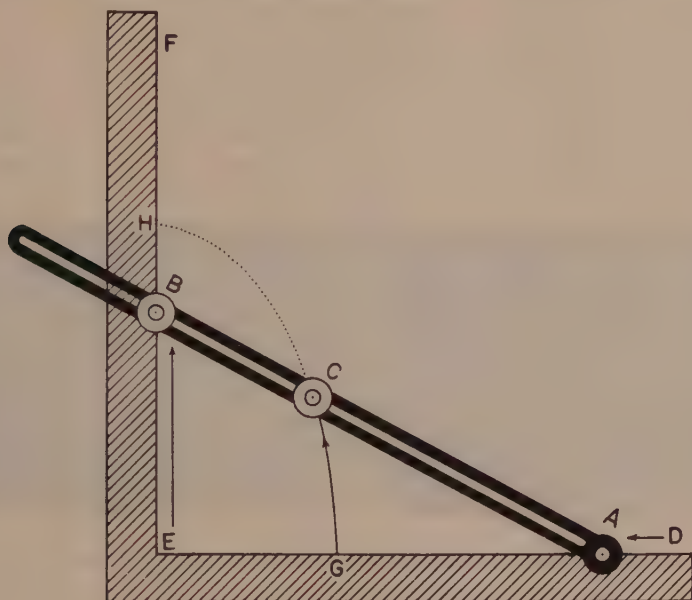


FIG. 1. Ellipsograph. An ellipse of any desired dimensions may be drawn, one quadrant at a time, by setting the distance AC equal to the semimajor axis, and the distance BC equal to the semiminor axis. Next, the two pins, A and B, are placed along one inside edge (DE) of a steel square aligned with the coordinate axes of the ellipse, with pin B at the corner E. Then, keeping the pins in contact with the edges of the square, A is moved from D to E, and B is moved from E to F. Point C inscribes the ellipse GH.

SKELETON INDICATRIX MODELS

The importance of the indicatrix in microscopical petrography has been emphasized by Wright,⁴ Tunell,⁵ and Rogers.⁶ Standard models of the indicatrix are mainly of the wooden or wire type, which leave much to the imagination. The transparent skeleton models (Fig. 2) described below have several advantages over the more elaborate wooden models. The principal circular and elliptical cross sections, representing indices of rays travelling parallel to optical and ellipsoidal axes, are all visible at

⁴ *Op. cit.* (Ref. No. 2).

⁵ Tunell, George, The ray-surface, the optical indicatrix, and their interrelation: an elementary presentation for petrographers. *Jour. Wash. Acad. Sci.*, vol. 23, pp. 325-338, 1933.

⁶ *Op. cit.* (Ref. Nos. 1 and 2).

the same time, without dismounting, and others may readily be visualized by interpolation. In addition, vibration directions and relative velocities of the different rays are shown by colored "arrows" normal to directions of propagation, and spaced at intervals inversely proportional to indices. Finally, the models are easily constructed and inexpensive.

For the uniaxial indicatrix, the circular section, the two principal elliptical sections, and an intermediate elliptical cross-section are shown. Following the practice of most textbook diagrams, this and other models



FIG. 2. Skeleton indicatrix models. The uniaxial model is at the left, the biaxial at the right.

are proportioned to represent imaginary minerals of greatly exaggerated birefringence, in order to emphasize the ellipsoidal form of the indicatrix. Suggested specifications are indicated in the diagram, Fig. 3, and are listed below:

- Two dovetailing ellipses,
Major axis—7 in.
Minor axis—4 in.
- Two semicircles, cut to dovetail with one of above ellipses,
Radius—4 in.
- One ellipse, dissected in 4 parts,
Major axis—5.2 in.
Minor axis—4 in.
- Thickness of celluloid throughout—.125 in.
- Spacing of lines representing vibration directions for:
 - O ray—10 mm. (blue)
 - E ray—6 mm. (red)
 - E' ray (travelling normal to intermediate ellipse)—8 mm. (brown)

The above specifications are for a uniaxial positive indicatrix; if desired, a similar model might be constructed for the negative indicatrix.

In marking vibration direction lines on the celluloid, a fairly deep groove is cut with the scriber, and left as rough as possible. This is filled with colored India ink from a fine-pointed pen, allowed to dry, and the

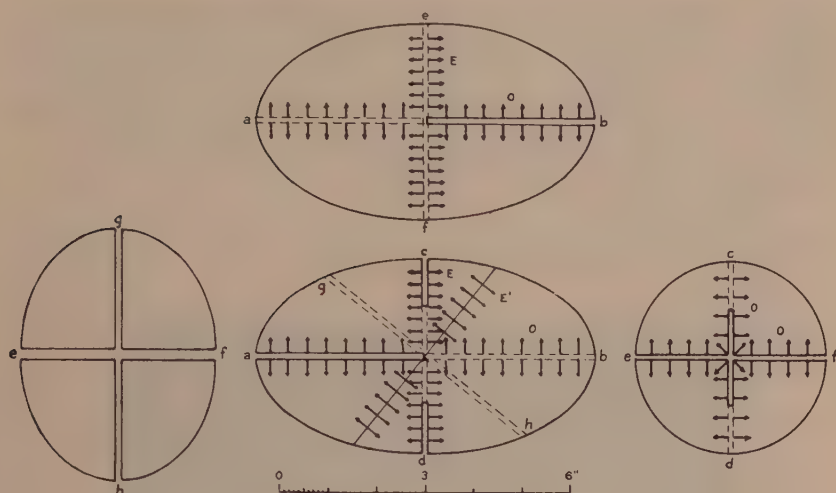


FIG. 3. Uniaxial indicatrix model, unassembled. Dashed lines indicate where parts fit together, and letters indicate how they fit.

inking repeated until the color is sufficiently strong. In assembling the model, dovetailing surfaces are coated with cement and then quickly slid together before the cement has time to dry. The joint is then further strengthened by applying one or more coats of cement externally.

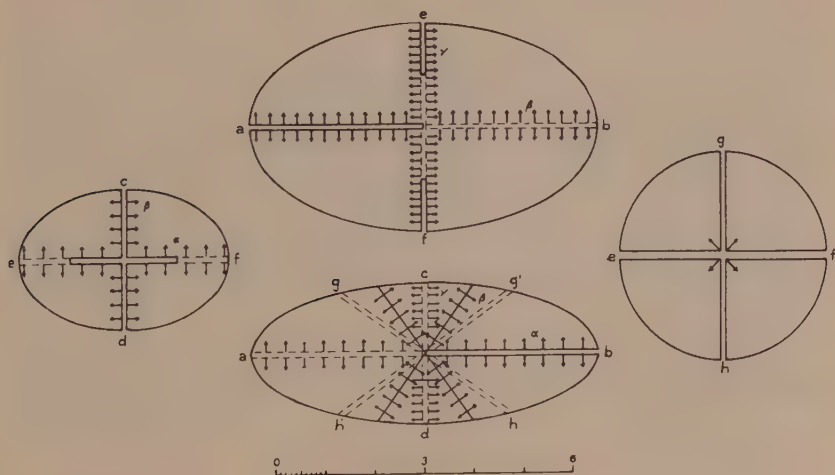


FIG. 4. Biaxial indicatrix model, unassembled.

For the biaxial indicatrix, the three principal elliptical cross-sections and the two circular sections are shown. Vibration directions and relative velocities are marked for rays travelling parallel to the two optical axes and the three ellipsoidal axes. Suggested specifications for the biaxial negative indicatrix are indicated in Fig. 4, and are listed below:

- One ellipse, of .125 in. celluloid,
 - Major axis—7 in.
 - Minor axis—4.2 in.
- One ellipse, of .125 in. celluloid, dovetailing with above,
 - Major axis—7 in.
 - Minor axis—2.8 in.
- One ellipse, of .125 in. celluloid, dovetailing with first ellipse above,
 - Major axis—4.2 in.
 - Minor axis—2.8 in.
- Two circles, of .08 in. celluloid, each dissected into four parts,
 - Radius—4.2 in.
- Spacing of vibration direction lines,
 - α —10 mm. (black)
 - β —7 mm. (red)
 - γ —4 mm. (blue)
- Axial angle—70°.

This model is assembled in the same way as that for the uniaxial indicatrix.

VIBRATION DIRECTIONS MODEL

In introducing students to the study of uniaxial minerals, the concept of vibration directions in relation to double refraction is readily demonstrated with calcite crystals and polaroid plates. For biaxial crystals, however, no correspondingly simple demonstration is readily available. In its stead, the writer has found it helpful to use a transparent celluloid model of an orthorhombic crystal (Fig. 5) which shows simply the vibration directions and relative velocities for light propagated through the crystal in different directions. These properties are represented by lines of different color and spacing on celluloid surfaces mounted within the crystal model, and corresponding to its three planes of symmetry. Fig. 6 shows the layout for the interior part of the model, and specifications are given below:

- Symmetry planes mounted inside crystal model:
 - 1 piece 4×5 in., to dovetail with
 - 1 piece 3×5 in.;
 - 2 pieces 3×1.96 in., to dovetail with above.

Spacing of vibration direction lines:

α —10 mm. (black)

β —7 mm. (blue)

γ —4 mm. (red)

Axial angle— 82° (negative)

Crystal model proper:

6 pieces cut to form an orthorhombic crystal $3 \times 4 \times 5$ in., inside measurement.

Thickness of celluloid—.08 in. throughout.

The core of the model, made up of the inscribed symmetry planes, is assembled first, and the crystal model built around it.



FIG. 5. Vibration directions model.

This model serves to illustrate the introductory discussions on biaxial minerals as presented by Winchell,⁷ and by Hartshorne and Stuart.⁸ By rotating the model around any one of the crystallographic axes, it may be seen that the index for the ray vibrating in the plane of that axis remains constant, while that for the ray vibrating in the plane normal to the axis varies between fixed values. Thus it is seen, as stated by Winchell,⁹ “not only that the indices are different for two rays of light traveling in the same direction, but vibrating in different directions, but

⁷ Winchell, A. N., *Elements of Optical Mineralogy*, Part I—Principles and Methods, 5th Ed., Wiley, New York, 1937, pp. 158–159.

⁸ Hartshorne, N. H., and Stuart, A., *Crystals and the Polarizing Microscope*, Arnold, London, 1934, pp. 74–75.

⁹ *Ob. cit.*, p. 159.

also that the indices are the same for rays traveling in different directions, but vibrating in the same direction. The direction of vibration, and not the direction of transmission, determines the index of refraction."

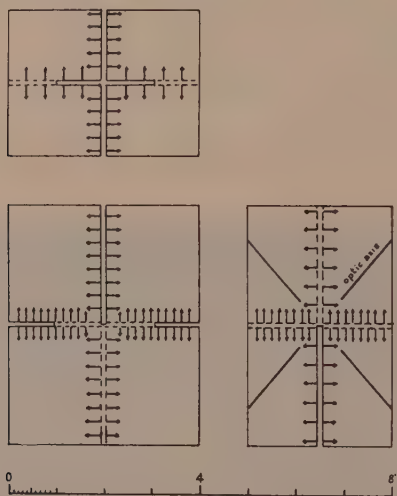


FIG. 6. Core of the vibration directions model, unassembled.

MODELS SHOWING RAY-SURFACES IN RELATION TO INDICATRIX

In discussions of optical theory, ray- or ray-velocity surfaces are commonly introduced, thus giving rise to a need for some means of showing the relation of these surfaces to the indicatrix. Following the usage of Rosenbusch and Wülfing,¹⁰ this may be done by showing both

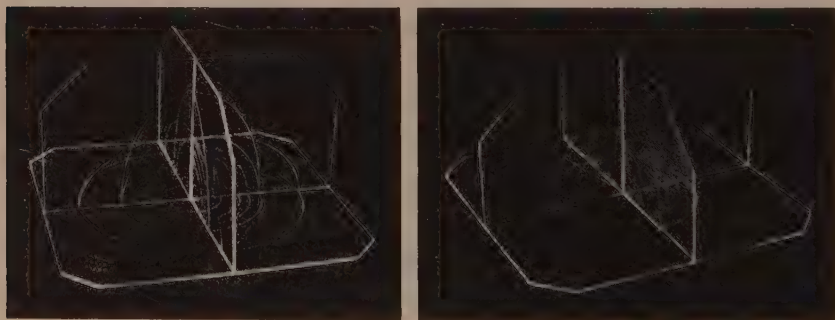


FIG. 7. Models showing relations of ray-surfaces to indicatrix. The uniaxial model is at the left, the biaxial at the right.

¹⁰ *Op. cit.* (Ref. 1), Figs. 82, 83, and 93.

with respect to a unit circle. Taking the radius of the circle as equal to one unit, the indicatrix is drawn, in the three mutually perpendicular cross-sections, by plotting numerical values of indices in the direction of *vibration*. The ray-surfaces are then drawn by plotting reciprocals of

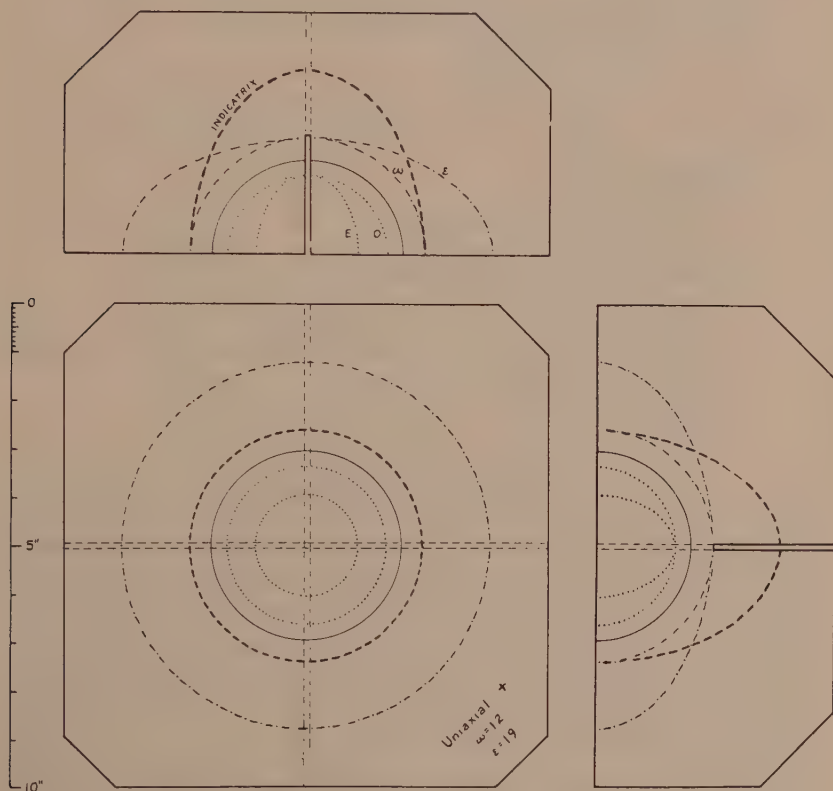


FIG. 8. Uniaxial ray-surface-indicatrix model, unassembled. The unit circle is shown by a light solid line. Dotted lines indicate ray-surfaces. The heavy dashed line represents the indicatrix. Dot and dash lines represent index surfaces. Light dashed lines show where parts fit together.

indices in the direction of *propagation*. If desired, index surfaces¹¹ may be shown by plotting values of indices in the direction of propagation; these are shown in the uniaxial model, but are omitted from the biaxial model in the interest of simplicity.

¹¹ Rosenbusch and Wülfing, *op. cit.*, pp. 91-92, 95-96, 108-109.

The uniaxial model is shown assembled in Fig. 7, and unassembled in Fig. 8. It is designed to represent an optically positive crystal of indices: $\omega = 1.2$, $\epsilon = 1.9$. Specifications are given below:

Base of .125 in. celluloid 10 in. square, inscribed with circles of the following radii:

- 2 in. (unit circle, blue)
- 1.63 in. (ray surface for O ray, black)
- 1 in. (ray surface for E ray, black)
- 2.4 in. (indicatrix and index surface for ω , red)
- 3.8 in. (index surface for ϵ , brown).

Two dovetailing upright pieces of .08 in. celluloid, each 5×10 in., and each inscribed with:

Semicircles of radii:

- 2 in. (unit circle, blue)
- 1.67 in. (ray-surface for O ray, black)
- 2.4 in. (index surface for ω , brown)

One semiellipse (ray-surface for E ray, black),

Semimajor axis—1.67 in.,

Semiminor axis—1 in.

Two semiellipses, one with major axis vertical (indicatrix, red), and one with major axis horizontal (index surface for ϵ , brown),

Semimajor axis—3.8 in.

Semiminor axis—2.4 in.

The two upright pieces are most conveniently laid out as a single sheet 10×10 in., which is sawed in two after the circles and ellipses are drawn. In cementing the upright pieces to the base, it is helpful to hold them in position by means of needle points hammered through the base so as to project upward about 1 mm., and then broken off below flush with the lower surface. These will prevent slipping while the cement is drying.

The biaxial model is shown unassembled in Fig. 9, and assembled in Fig. 7. Specifications below are for a model representing an optically positive crystal of indices 1.2, 1.4, and 2.0.

Base (XY section) of .125 in. celluloid 10 in. square, inscribed with:

Circles of radii:

- 2 in. (unit circle, blue)
- 1 in. (ray surface for slow ray, black)

One ellipse (ray surface for fast ray, black),

Semimajor axis—1.67 in.

Semiminor axis—1.43 in.

One ellipse (indicatrix, red),

Semimajor axis—2.8 in.

Semiminor axis—2.4 in.

Upright (XZ section) of .08 in. celluloid, 5×10 in., inscribed with:

Semicircles of radii:

- 2 in. (unit circle, blue)

1.43 in. } ray-surfaces, black

Semiellipse,

- Semimajor axis—1.67 in.
 Semiminor axis—1 in.
 Semiellipse (indicatrix, red),
 Semimajor axis—4 in.
 Semiminor axis—2.4 in.
 Optic axes (primary, red) with axial angle of 79° .
- Upright (YZ section) of .08 in. celluloid 5×10 in., dovetailing with above, and inscribed with:
- Semicircles of radii:
 2 in. (unit circle, blue)
 1.67 in. } ray-surfaces, black
 Semiellipse, }
 Semimajor axis—1.43 in.
 Semiminor axis—1 in.
- Semiellipse (indicatrix, red),
 Semimajor axis—4 in.
 Semiminor axis—2.8 in.

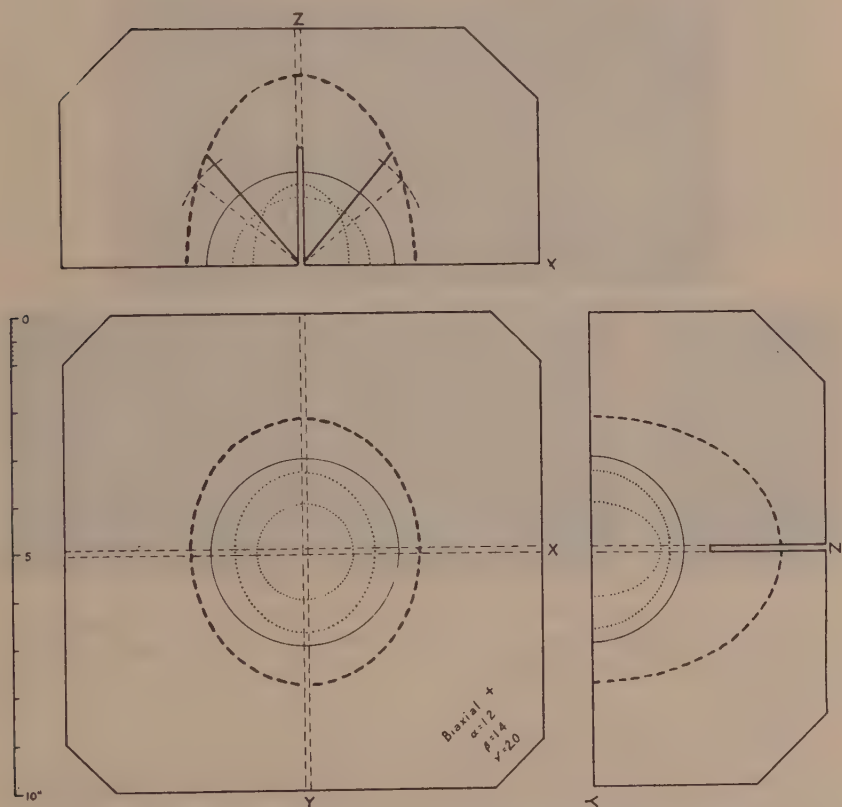


FIG. 9. Biaxial ray-surface-indicatrix model, unassembled. The unit circle is shown by a light solid line, the ray-surfaces by dotted lines, the indicatrix by a heavy dashed line, the primary optic axes by heavy solid lines, and the traces of the circular section on the XZ plane by dot and dash lines.

On the XZ upright section, traces of the circular sections are located by finding the intersections of a circle of radius 2.8 in. (β) with the indicatrix. The optic axes are drawn perpendicular to the traces of the circular sections. The model is assembled in the same way as that for the uniaxial crystal: circles and ellipses are inscribed on the upright pieces before they are sawed apart, then these two pieces are dovetailed together, and finally they are cemented to the base.

MODELS SHOWING ORIENTATION OF THE INDICATRIX IN THE CRYSTAL

In studying mineral grains in oil immersion or in thin section, it is generally desirable to note the orientation of the indicatrix in each grain

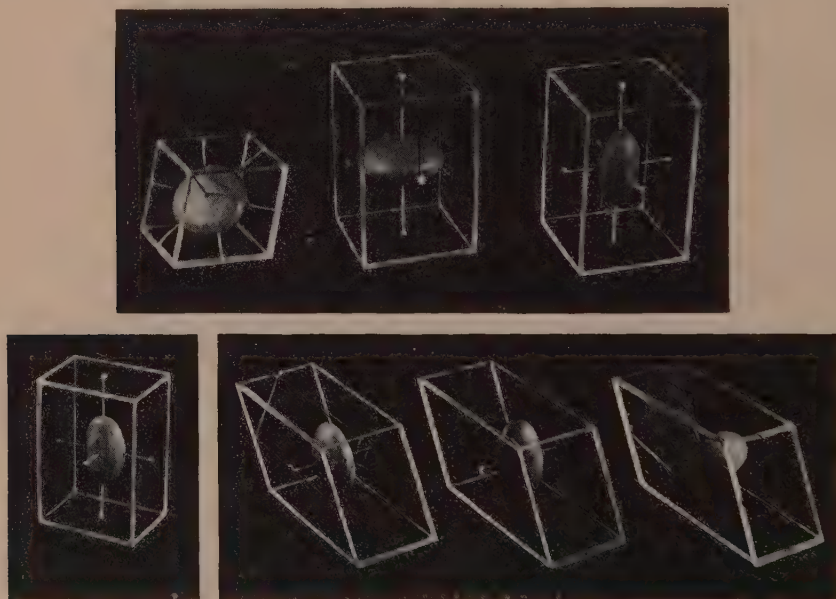


FIG. 10. Models showing orientation of the indicatrix in different crystals. Top row, left to right: rhombohedral negative; tetragonal negative; tetragonal positive. Bottom row, left to right: orthorhombic, $X=a$; $Z=c$; monoclinic, $X=b$; monoclinic, $Y=b$; monoclinic, $Z=b$.

examined. To aid in visualizing the different possible orientations and their relations to cleavages and to crystal faces, wooden indicatrix models are mounted inside celluloid crystal models (Fig. 10).

For uniaxial crystals, positive and negative tetragonal, hexagonal, and rhombohedral models may be constructed. Specifications are given below:

Crystal models:

Tetragonal— $2.5 \times 2.5 \times 4$ in., inside measurementHexagonal— $1.4 \times 1.4 \times 1.4 \times 4$ in., inside measurementRhombohedral— $2 \times 2 \times 2$ in., inside measurement, with acute angle of 79° between edges of sides

Thickness of celluloid—.08 in.

Indicatrices:

Prolate ellipsoids of revolution,

Axes 2 in. and 1 in.

Oblate ellipsoids of revolution,

Axes 1.8 in. and 1 in.

The wooden ellipsoids are made of gum wood or some other fine-grained, moderately hard wood, and are cut to shape on a woodworking lathe. Holes corresponding to the crystallographic axes are drilled through the wood *before* turning to shape, and are aligned so as to *just miss* one another at the center. These holes should be about $1/16$ in. in diameter. After receiving a coat of varnish or shellac, the ellipsoids are mounted inside the crystal models, which are completely assembled except for the top. String of one color is used to represent the horizontal crystallographic axes, and string of a different color to represent the vertical axis. The string is doubled, threaded through the ellipsoid and the crystal model, knotted at both ends, and then tightened by twisting and fixed in position by coating the knots with celluloid cement.

For biaxial crystals, orthorhombic and monoclinic models showing different ellipsoidal orientations were constructed. For orthorhombic crystals, six different models are necessary to show all possible orientations of the indicatrix. One of these is shown in Fig. 10. Crystal models $2 \times 2.8 \times 4$ in., inside measurement, are used. The ellipsoids are triaxial, with major, intermediate, and minor axes of 1.8, 1.2, and .8 in., respectively. These are made from ellipsoids of revolution by carefully sanding them to triaxial form by hand. String of three different colors is used in mounting the ellipsoids inside the crystal models.

For monoclinic crystals, three models suffice to show all possible orientations of the indicatrix. In these three models, the three axes of the ellipsoid, respectively, are mounted on thin metal rods, which, in turn, are mounted in the crystal models to correspond to the *b* crystallographic axis, with projecting ends bent over to provide a means of turning the wooden model inside the crystal. Thus the two remaining ellipsoidal axes may be rotated into any desired angular relation with the *a* and *c* crystallographic axes. The monoclinic crystal models are $2 \times 2.8 \times 4.2$ in., inside measurements and show the clino axis making an angle of 60° with the plane of the other two axes.

In any of the biaxial models described above, prism faces in addition

to pinacoids may be represented by means of colored lines inscribed on the inside of the model.

UNIVERSAL STAGE MODEL

In demonstrating the manipulation of the universal stage, a large scale model is helpful. Such a model (Fig. 11) is easily constructed from a disc of .125 in. celluloid. Fig. 12 gives dimensions and details. All working parts of the model are cut as concentric rings from the single



FIG. 11. Universal stage model.

disc. Rings are hinged together by means of heavy darning needles forced into drill holes barely large enough to receive them. Rings designed to rotate concentrically within others are held in place by four paired sets of projecting arms. Angular distances around the rings may be marked off in units of 10° or less, if desired. The completed assembly is mounted over a wooden base to which two upright arms are affixed. In using this model, wooden indicatrix models, like those used in the crystal models, may be attached to the inner ring with modeling clay or adhesive.

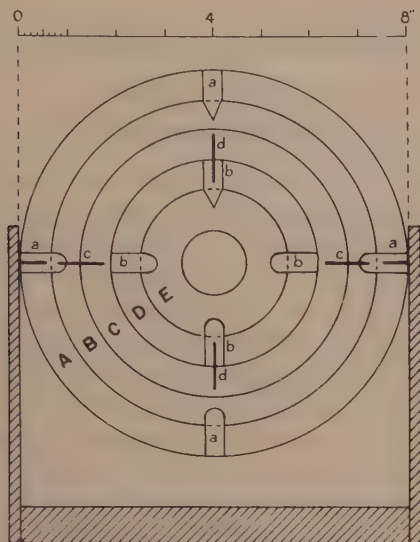


FIG. 12. Diagram showing assembly of universal stage model. Ring *A* is hinged to the sides of the frame. Ring *B* rotates concentrically within *A*, being held in place by the arms *a*. Ring *C* is hinged to *B* at *c*. Ring *D* is hinged to *C* at *d*. Ring *E* rotates concentrically within *D*, being held in place by the arms *b*. The center of ring *E* is cut out, in order to accommodate a small wooden indicatrix model.

CONCLUDING STATEMENT

The foregoing descriptions of models are intended to be suggestive rather than definitive. Numerous modifications in detail may suggest themselves to the reader, either to improve the models or to adapt them for specific objectives. Furthermore, a wide field remains for the designing of additional models to illustrate further particulars of optical theory and of petrographic practice. Some of these might well be suggested by perspective drawings in textbooks. Certainly the value of visual models in saving time and increasing the efficiency of teaching more than justifies the time and effort expended in designing them.

CRYSTALLOGRAPHY OF MEYERHOFFERITE

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The calcium borate meyerhofferite was first described by W. T. Schaller (1916) and nothing has since been published concerning its crystal form. Numerous specimens of this and other borates were collected at the original locality by W. F. Foshag and F. A. Gonyer in 1930. A series of these was presented to the Harvard Mineralogical Museum, and examination of this material has revealed new crystallographic data which seem to merit publication, especially as they seem to justify a modification of Schaller's original crystal elements.

His description of meyerhofferite was based on crystals formed on or within fibrous pseudomorphs after inyoite. Similar pseudomorphs of great perfection are included in the new collections. There are also masses of interlaced glassy crystals of meyerhofferite embedded in a hard yellow clay, their interstices filled by snow-white fibrous aggregates of a later generation of meyerhofferite. It was from these masses that the newly studied crystals were obtained. Most of the hundreds of crystals examined were of the simple form described as typical by Schaller: prismatic crystals terminated by three forms in the macrodome zone and a single pyramid. A small number of the crystals, however, presented other terminal faces including a number of pyramids.

Meyerhofferite is triclinic and Schaller so orientated the crystal that the single observed pyramid should be $\{111\}$. This position unfortunately made the basal pinacoid $\{001\}$ slope to the rear. With the finding of pyramids in other quadrants of the crystal there seemed no good reason for maintaining this unusual position, so that the crystals of meyerhofferite are described in this paper as rotated 180° about the vertical axis from the position of Schaller.

It was observed that many of the more highly modified crystals showed a more or less curved solution surface in a quadrant diagonally opposed to that containing the common pyramid. This rounded surface sometimes developed into two facets, still rather imperfect in quality; but crystals were finally found in which these faces were measurable on the goniometer. It would appear that the general direction of what has been here adopted as the pyramid $\{111\}$ is peculiarly sensitive to solution attack.

Fourteen crystals were measured completely. The perfect cleavage parallel to $\{010\}$ was rarely absent and served as a means of establishing the v_0 of each crystal. The prism zone was generally of good quality and

in no case was any prism form observed besides $\{110\}$ and $\{\bar{1}\bar{1}0\}$. The position angles of the forms present on the 14 crystals were collected and their mean values taken. These average angles were very similar to the average angles recorded in Schaller's paper. It was therefore regarded as best to combine the two sets of measurements in an average, weighted for the number of observations of each form. In Table 1 these figures are shown, Schaller's values for ϕ being adjusted to the new position above mentioned. Table 2 contains the observations of new pyramids of which one, $u\{\bar{1}11\}$ was found frequently and in excellent position.

TABLE 1. MEASURED ANGLES OF MEYERHOFFERITE

Form	No. of measurements	Schaller		Palache			Weighted mean		
		ϕ	ρ	No.	ϕ	ρ	No.	ϕ	ρ
<i>c</i> 001	6	90° 13'	11° 48'	5	89° 27'	11° 56'	11	89° 52'	11° 51½'
<i>a</i> 100	26	93 12	90 00	14	93 05	90 00	40	93 09½	90 00
<i>m</i> 110	19	54 15	90 00	11	54 19	90 00	30	54 16½	90 00
<i>M</i> 110	13	129 49	90 00	18	129 39	90 00	31	129 43	90 00
<i>y</i> 101	9	93 00	50 22	12	92 29	50 26	20	92 41½	50 24½
<i>t</i> 101	9	— 85 59	38 35	12	— 85 49½	38 22	21	— 85 53½	38 27½
<i>p</i> 111	9	—132 26	46 54	15	—132 30	46 53	24	—132 28½	46 53

TABLE 2. MEASURED ANGLES OF NEW FORMS ON MEYERHOFFERITE

Form	No. of faces	Quality	ϕ ρ		Range	
			ϕ	ρ	ϕ	ρ
<i>u</i> 111	5	excellent	— 43° 20'	48° 53'	43° 27'—43° 08'	48° 42'—49° 07'
<i>o</i> 111	2	poor	57 58	54 05	Many other observations in this general vicinity—faces rounded.	
<i>E</i> 212	1	poor	76 32	51 13		
<i>D</i> 212	1	good	—112 55	40 22		

On the basis of these combined data, elements were calculated with results which are presented in the heading of Table 3. The new elements correspond very nearly to those of Schaller as was to be expected. The same is true of the position angles of the forms which appear in the same table. Those forms described by Schaller, which he found but once have been omitted from this table. The table also contains the angles made

by each form to the three pinacoids, *B*, *C* and *A*, a negative sign before *B* or *A* indicating that the face is nearest to the negative end of the normal to (010) or (100), respectively.

TABLE 3. MEYERHOFFERITE— $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$

Triclinic; pinacoidal—I

$a:b:c=0.7904:1:0.7763$; $\alpha=90^\circ 41'$, $\beta=101^\circ 51'$, $\gamma=86^\circ 44'$ $p_0:q_0:r_0=0.9837:0.7610:1$; $\lambda=89^\circ 49'$, $\mu=78^\circ 10\frac{1}{2}'$, $\nu=93^\circ 11\frac{1}{2}'$ $p_0'=1.0051$ $q_0'=0.7775$ $x_0'=0.2098$ $y_0'=0.0003$					
Form	ϕ	ρ	A	B	C
<i>c</i> 001	$89^\circ 55\frac{1}{2}'$	$11^\circ 51'$	$78^\circ 10\frac{1}{2}'$	$89^\circ 59'$	$0^\circ 00'$
<i>b</i> 010	0 00	90 00	$93^\circ 11\frac{1}{2}'$	0 00	$89^\circ 59'$
<i>a</i> 100	$93^\circ 11\frac{1}{2}'$	90 00	0 00	$93^\circ 11\frac{1}{2}'$	$78^\circ 10\frac{1}{2}'$
<i>k</i> 370	29 43	90 00	$63^\circ 28\frac{1}{2}'$	29 43	$84^\circ 08\frac{1}{2}'$
<i>A</i> 350	38 59	90 00	$54^\circ 12\frac{1}{2}'$	38 59	$82^\circ 34'$
<i>m</i> 110	54 17	90 00	$38^\circ 54\frac{1}{2}'$	54 17	$80^\circ 23\frac{1}{2}'$
<i>n</i> 520	$75^\circ 44\frac{1}{2}'$	90 00	17 27	$75^\circ 44\frac{1}{2}'$	78 31
<i>s</i> 310	$78^\circ 33\frac{1}{2}'$	90 00	$14^\circ 38\frac{1}{2}'$	$78^\circ 33\frac{1}{2}'$	$78^\circ 23\frac{1}{2}'$
<i>r</i> 810	87 39	90 00	$5^\circ 32\frac{1}{2}'$	87 39	$78^\circ 09\frac{1}{2}'$
<i>h</i> 3 $\bar{1}$ 0	107 26	90 00	$14^\circ 14\frac{1}{2}'$	107 26	$78^\circ 42\frac{1}{2}'$
<i>w</i> 4 $\bar{3}$ 0	$122^\circ 29\frac{1}{2}'$	90 00	29 18	$122^\circ 29\frac{1}{2}'$	80 02
<i>M</i> 1 $\bar{1}$ 0	129 43	90 00	36 31	129 43	$80^\circ 55\frac{1}{2}'$
<i>v</i> 3 $\bar{5}$ 0	143 25	90 00	50 13	143 25	82 59
<i>y</i> 101	92 38	50 32	39 28	92 02	38 42
<i>t</i> 1 $\bar{0}$ 1	$-85^\circ 56\frac{1}{2}'$	$38^\circ 30\frac{1}{2}'$	$128^\circ 30\frac{1}{2}'$	$92^\circ 31\frac{1}{2}'$	50 20
<i>f</i> $\bar{6}$ 05	$-86^\circ 07'$	$44^\circ 54\frac{1}{2}'$	$133^\circ 54'$	92 44	56 44
<i>g</i> $\bar{5}$ 04	$-86^\circ 09'$	46 19	$136^\circ 18\frac{1}{2}'$	92 47	$58^\circ 08\frac{1}{2}'$
<i>o</i> 111	59 15	$54^\circ 41\frac{1}{2}'$	$47^\circ 23\frac{1}{2}'$	$65^\circ 20\frac{1}{2}'$	44 47
<i>E</i> 212	74 39	$51^\circ 31\frac{1}{2}'$	42 05	$78^\circ 02\frac{1}{2}'$	49 49
<i>u</i> 1 $\bar{1}$ 1	$-43^\circ 35\frac{1}{2}'$	$49^\circ 01\frac{1}{2}'$	123 23	56 51	57 39
<i>p</i> 1 $\bar{1}$ 1	$-132^\circ 15\frac{1}{2}'$	$47^\circ 00\frac{1}{2}'$	120 52	119 28	$56^\circ 12\frac{1}{2}'$
<i>D</i> 2 $\bar{1}$ 2	$-112^\circ 43\frac{1}{2}'$	40 43	$125^\circ 55\frac{1}{2}'$	104 24	51 49

The orientation of the indicatrix, determined by Dr. F. H. Pough from a single crystal mounted on a universal stage, is as follows:

	ϕ	ρ	
X	$165^\circ 00'$	$62^\circ 00'$	$2V=78^\circ$
Y	45 30	47 00	
Z	$-83^\circ 00'$	55 00	

A stereographic projection of the indicatrix is given in figure 3.

The structural lattice constants have been determined by Mr. George Switzer upon these newly studied crystals. Because of the quality of the material it was possible to determine all of the unit cell dimensions by x-ray methods with considerable accuracy. Rotation, zero-layer and first-layer Weissenberg photographs were taken with $c[001]$ as the axis

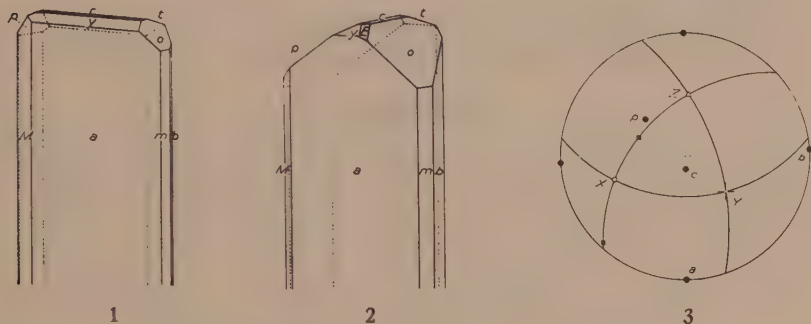


FIG. 1. Meyerhofferite: typical crystal in new position.

FIG. 2. Meyerhofferite: more complex crystal, showing two new forms $o\{111\}$ and $E\{212\}$.

FIG. 3. Meyerhofferite: stereogram of the optical indicatrix. (After F. H. Pough.)

of rotation, and rotation and zero-layer photographs about the $a[100]$ and $b[010]$ axes. From the zero layer photographs about each of the three crystallographic axes, two values for each of the unit spacings between the pinacoidal planes were obtained, and also the planar spacings of (110) , $(10\bar{1})$, and (011) . From the average values of these spacings were then calculated the reciprocal lattice constants a^* , b^* , c^* , α^* , β^* , γ^* , which in turn yielded the following unit cell dimensions:

$$a_0 = 6.60 (\pm 0.02) \text{ \AA} \quad \alpha = 91^\circ 00' (\pm 0^\circ 05')$$

$$b_0 = 8.33 (\pm 0.02) \quad \beta = 101^\circ 31' (\pm 0^\circ 05')$$

$$c_0 = 6.48 (\pm 0.02) \quad \gamma = 86^\circ 55' (\pm 0^\circ 05')$$

$$a_0 : b_0 : c_0 = 0.792 : 1 : 0.778$$

The unit cell volume then becomes 348.83 cubic $\text{\AA}$, and with the density 2.12 given by Schaller (1916), the molecular weight of the unit cell $M = 448.18$.

Table 4 gives the atomic content of the unit cell, using the average of two analyses by Schaller.

TABLE 4. ANALYSIS OF MEYERHOFFERITE AND CONTENT OF UNIT CELL

	1	2		3		4	5
CaO	26.45	25.30	0.4512	$2 \times .226$		2.17	2
B ₂ O ₃	46.40	46.09	0.6618	$3 \times .221$		2.97	3
H ₂ O	28.76	28.61	1.5895	$7 \times .227$		7.12	7

1. Analysis by W. T. Schaller (1916).

2. Analysis calculated to 100%.

3. Molecular ratios.

4. Atomic content of the unit cell, from $M=448.18$.

5. Theoretical unit cell content, expressed by the formula (Ca₂B₆O₁₁ · 7H₂O).

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CRYSTALLOGRAPHY OF BRAUNITE FROM NAGPUR, INDIA

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INTRODUCTION

The Karabacek Collection of the Harvard Mineralogical Museum contains some excellent specimens of crystallized braunite ($3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$) from Nagpur, India, which seem to merit a description both because of their quality and their unusual habit. Fermor (1909) has previously given an incomplete crystallographic description of braunite from this locality in his work on the manganese deposits of India.

MORPHOLOGY

Choice of setting. Braunite is tetragonal holohedral and has, therefore, two possible choices of the a crystallographic axes. It has been set up in both of these two possible positions by various investigators. Dana (1892) chose a pseudo-isometric setting with $c=0.9922$. Goldschmidt (1897) chose the alternative setting, with $c=1.4032$.

Aminoff (1931) made an x -ray investigation of braunite from Långban, Sweden. He took rotation photographs about the c axis and the two possible a axes, and by means of the usual criteria determined the Goldschmidt setting to be correct. Rotation, and zero- and first-layer line Weissenberg photographs of braunite from Nagpur, with $c[001]$ as the rotation axis, were taken by the writer, whose work is in agreement with that of Aminoff. Table 1 summarizes the results obtained.

TABLE 1. STRUCTURAL LATTICE CONSTANTS OF BRAUNITE

	<i>Aminoff</i>	<i>Switzer</i>
a_0	13.43 Å	13.23 Å
c_0	18.93	18.77
c_0/a_0	1.404	1.415

The Goldschmidt setting for braunite is therefore correct and has been used in the following crystallographic description. The transformation from Dana to Goldschmidt is obtained by the formula $110/\bar{1}10/002$ and from Goldschmidt to Dana by $1\bar{1}0/110/001$.

Crystallography. Nagpur braunite is black and massive with occasional crystal-lined cavities which may or may not be filled with calcite. The crystals are usually small (less than 3 mm.), and the largest are not over 8 mm. in length. The crystals selected for measurement were from $\frac{1}{2}$ to 2 mm. in length, singly terminated, and of very good quality.

Four crystals were measured completely and several others examined and their forms identified. The morphological elements were calculated from the three best crystals. The forms $e\{011\}$ and $x\{131\}$ were best developed and most often present and were used for the calculations. Table 2 gives the range of the measured values and the morphological elements obtained from the measured mean for the forms $e\{011\}$ and $x\{131\}$ of three crystals.

TABLE 2. CALCULATION OF MORPHOLOGICAL ELEMENTS

Form	No. of readings	Measured range				Measured mean		$p_0=c$
		ϕ		ρ		ϕ	ρ	
$e\{011\}$	11	-0°05'	to 0°08'	54°30'	to 54°41'	0°00'	54°36'	1.4071
$x\{131\}$	18	18 15	to 18 28	77 14	to 77 24	18 26	77 20	1.4069
Average value $p_0=1.4070$								

Habit. Nagpur braunite occurs in two distinct habits. The more common habit has the ditetragonal pyramid $x\{131\}$ as the dominant form, with the prism and base very small or lacking; $e\{011\}$ is always present but is smaller than $x\{131\}$. Various other forms are present as small truncating edges.

The second habit is typified by a dominance of $e\{011\}$ with $c\{001\}$ or $x\{131\}$ as the second largest form, and various other truncating forms.

Combination of forms. Below is given the combinations of forms observed on six crystals, listed in order of decreasing dominance. The form letters used are those adopted by Koechlin (1913). (See angle table for the complete form list.)

1. x, y, e, c, n
2. $x, e, y, \tau, n, d, \epsilon, w$
3. x, e, y, m, τ, n, d
4. x, n, e, y, m
5. $x, e, y, c, n, \gamma, \tau$
6. e, x, c, i, g

TABLE 3. BRAUNITE— $3 \text{ Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$
Tetragonal; ditetragonal-dipyramidal— $4/m \ 2/m \ 2/m$
 $p_0 = c = 1.4070$

Forms	ϕ	ρ	A	$\bar{M}$
<i>c</i> 001	—	0°00'	90°00'	90°00'
<i>a</i> 010	0°00'	90 00	90 00	45 00
<i>m</i> 110	45 00	90 00	45 00	90 00
τ 013	0 00	25 07½	90 00	72 31½
γ 012	0 00	35 07½	90 00	65 59½
<i>e</i> 011	0 00	54 36	90 00	54 48
<i>s</i> 021	0 00	70 26	90 00	48 13
<i>o</i> 338	45 00	36 44	64 59	90 00
<i>q</i> 5.5.12	45 00	39 39½	63 10½	90 00
<i>n</i> 112	45 00	44 51	60 05	90 00
<i>p</i> 111	45 00	63 19	50 49	90 00
<i>l</i> 221	45 00	75 53½	46 22	90 00
<i>r</i> 331	45 00	80 29½	45 44	90 00
<i>b</i> 441	45 00	82 50½	45 33½	90 00
<i>D</i> 177	8 08	54 52	83 21½	60 37
<i>g</i> 135	18 26	41 40	77 52	72 42
σ 155	11 18½	55 07½	80 44½	62 55½
<i>i</i> 134	18 26	48 02½	76 24	70 34½
<i>y</i> 133	18 26	56 00½	74 48	68 14
<i>u</i> 153	11 18½	67 18½	79 34½	59 13
<i>t</i> 378	23 12	53 15½	72 41	72 39
λ 5.11.13	24 26	52 27½	70 49	73 47½
<i>v</i> 122	26 34	57 33½	67 49½	74 31½
<i>d</i> 142	14 02	70 58½	76 45	60 53½
<i>f</i> 344	36 52	60 22½	52 04½	82 56
ϵ 353	30 58	69 55	61 06	72 10
<i>w</i> 121	26 34	72 22	64 46½	72 27½
π 131	18 26	77 20	72 02	64 07½
η 151	11 18½	82 04	78 48	56 40½
<i>j</i> 241	26 34	80 58	63 47½	71 48

Rare and doubtful:

ρ 175	8.14.3	571
μ 343	δ 351	11.13.1

Twinning. One specimen of the material examined exhibited numerous small twinned crystals of braunite, the twin plane being $\{112\}$. Since the plane $\{112\}$ has $\rho = 44^\circ 51'$, the faces of the form $e\{011\}$ of the two individuals of a twin are almost coplanar. The calculated angular difference between them is $0^\circ 18'$. The measured angle on one crystal of fair quality was $0^\circ 33'$. Figure 3 illustrates a typical twin.

Angle table. The elements accepted by Goldschmidt and Dana are based on measurements by Flink (1891). Flink gives little of the quality of his measurements, and all are zonal, and without statement of the number of observations. Therefore, it seems safe to conclude that the elements obtained from the Nagpur crystals are based on superior data, and they have been used as the basis of a new angle table. The form list is that of Koehlin (1913) with the modification that forms seen only once, or forms seen twice but in poor position are considered "rare and doubtful." The columns A and $\bar{M}$ give the interfacial angles to the faces (100) and $(\bar{1}10)$ respectively, which is a new usage. These two angles, as shown in the diagram, figure 4, give angles comparable to the pinacoidal angles of the orthorhombic system (Peacock 1934), and also by a simple calculation the important interfacial angles.

$$\begin{aligned} A &= (100):(hkl) \\ 90-A &= \frac{1}{2}(hkl:\bar{h}kl) \\ \bar{M} &= (\bar{1}10):(hkl) \\ 90-\bar{M} &= \frac{1}{2}(hkl:khl) \end{aligned}$$

The order of listing the forms is established as follows: (1) pinacoids, (2) prisms, (3) 2nd order pyramids, (4) 1st order pyramids, (5) ditetragonal pyramids according to increasing values of the ratio h/l (x co-ordinate) of the face (hkl) in gnomonic projection.

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ALUMINUM AND SILICOSIS

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ABSTRACT

Experiments are described to show that aluminum behaves chemically toward silica under suitable conditions in a manner similar to that of mineral protectors described earlier in this Journal.

INTRODUCTION

The paramount importance of silicosis to industry, classified by some authorities as the leading industrial disease today, has by its impact overcome much of the inertia once so prevalent in the general attitude toward it. An early development, and one to be credited with real success, is that of dust elimination, though it is really dust reduction only. The limitation of this procedure is the high cost, especially of removing the finest fraction, with the all too common result that this remains. Many regard this last trace of dust as the most harmful. Admixed mineral protector dusts have been suggested to render harmless this fine material, thereby requiring elimination only of the more easily and cheaply removed first fraction. This paper is concerned with these protector dusts.

In an earlier paper to which the senior writer contributed,¹ a mineralogic explanation of protectors was offered. Since then Denny, Robson and Irwin have discovered the protective influence of aluminum and in announcing their discovery have suggested a wholly different explanation.² We feel that it is essential to the proper use of a protector to understand the principles of its operation. To that end we are disagreeing with the *explanation* of Denny, Robson and Irwin, while accepting the conclusions of their animal experiments that *aluminum is a protector*. Our subject matter is therefore unavoidably controversial. Our purpose is to show (1) that the presence of aluminum, as a protector substance does not decrease the solubility of silica in aqueous solution, but that it removes dissolved silica from solution, (2) that this effect of aluminum on dissolved silica is not the basis of its protective capacity, (3) that the basis of the protective capacity of aluminum is its ability to flocculate colloidal silica as do other protector substances described earlier in this journal, and (4) that certain reactions of aluminum and the alkaline earth carbonates toward silica are similar.

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THE PROBLEM

The literature on silicosis has credited the property of protection to the following: shale,³ carbon, the alkaline earth carbonates,¹ iron oxide,^{1,4} gypsum,⁴ and Portland cement.⁵ It has been suggested that the essential protective feature of these substances is their ability to flocculate silica, based on the charge which they carry in the appropriate medium, rather than to inhibit solution of silica. Aluminum is shown by an electrophoresis test to carry a charge in dilute sodium chloride solution similar to that of the protectors listed above, and we believe therefore that it acts as a protector in a manner comparable to these substances. This is an important distinction, since the effective practical use of any protector is made possible by an understanding of the principle on which it operates. If, for instance, the protection afforded by aluminum is dependent on its capacity to inhibit the solubility of silica as Denny, Robson and Irwin believe, then we are dealing with a rather specific property which would be expected to vary in effectiveness with the nature of the siliceous material. In this case it would be necessary to determine its specific protective capacity against each noxious element of industrial dusts. But if the protective influence is like that of the other protectors listed, that is, dependent on its ability to flocculate silica, then its protective capacity apparently covers all siliceous materials which hydrate or dissolve under the conditions in which we are interested and release colloidal silica. Furthermore, additional potential protectors, may be found by first making electrophoresis tests on colloidal suspensions of the materials under consideration.

Protectors, as we understand them, flocculate disperse material in body fluids, as they are known to do in laboratory solutions. This flocculation is tantamount to a reduction in the number of discrete units to be phagocytosed.† This function of protector materials is outlined in an earlier paper to which the interested reader is referred.¹

The experiments of Denny, Robson and Irwin show that aluminum protects animals against silicosis. They explain this protection by stating that "the addition of small quantities of aluminum dust almost completely inhibits the solubility of siliceous material in the beaker." They define solubility as "... the concentration of silica in solution obtained under the conditions noted." They determine the silica in solution "colorimetrically by the method of King and Dolan." The colorimetric method of King and Dolan indicates silica in the soluble form almost exclusively as distinct from particulate or colloidal silica.⁶ An absolutely sharp distinction is of course never possible since ordinarily colloidal

† An analogy may be drawn to opsonization.

silica is contributing to the amount of silica in solution. The analytical results of Denny, Robson and Irwin being thus concerned with dissolved silica do not take into consideration the particulate silica. But suspicion rests heavily on particulate silica as the cause of silicosis. This view is not only widely held but was convincingly expressed in 1936 by F. G. Banting,⁷ who, after describing experiments performed in his laboratory, says, "These experiments show that when silica is in the soluble form it is readily transported in the blood stream, and, since it is rapidly excreted by the kidneys, it does not produce fibrosis." And again he says, "It would therefore appear that fibrous nodules form as a result of particulate silica and not of dissolved silica." Denny, Robson and Irwin state that "Gye and Purdy were the first to point out that the chemical reaction and not the physical presence of siliceous material was responsible for the production of the fibrosis in silicosis." Gye and Purdy used colloidal silica in their experiments, the results of which were published under the title, "The Poisonous Properties of Colloidal Silica." There is no known quantitative relationship between the dissolved silica revealed by colorimetric analysis and the particulate silica present in any one solution. It would seem inadvisable, therefore, to attempt to explain the protective influence of aluminum solely on its effect on the dissolved silica revealed by colorimetric analysis. Attention may be called to a most significant statement by Gye and Purdy pertaining to the effect of colloidal silica on rabbits. They say⁸—"We have come therefore to regard the dose of 5 mgm . . . as being on the borderline of poisonous doses. *This applies only to freshly prepared highly dispersed sol; in older preparations of silica sol in which aggregation has occurred much larger doses may be given without producing lesions.*" (The italics are ours.) In other words, silica in the flocculated state—the objective of a protector—lacks potency. It is possible that a part of the reduced effect of the "older preparations" is to be attributed to an increase in the proportion which is in solution and a corresponding decrease in the quantity of colloid, though the authors do not formally mention it.

RELATIONSHIP OF ALUMINUM TO DISSOLVED SILICA

Let us examine the "beaker experiment" of Denny, Robson and Irwin, namely, that two identical samples of silica, one with aluminum, are treated with water and filtered—the filtrate from aluminum and silica contains no silica, the other does. We suggest that the silica has been equally dissolved in both cases, but the aluminum present in the one has removed the silica from solution by adsorption or chemical combination. The silica thus tied to the aluminum does not pass through the filter paper and does not appear in the analysis of the filtrate. We shall

prove this statement experimentally and show that not merely aluminum, but similarly any one of several metallic ions (such as, magnesium, calcium, zinc, tin, iron or nickel) which, like aluminum, forms a relatively insoluble flocculent hydroxide in mildly alkaline solution is capable of removing silica from that solution.

We duplicated the "beaker experiment" of Denny, Robson and Irwin to assure ourselves that we were employing essentially the same technique. Following their procedure, we then prepared a silica solution by agitating one gram of -10 micron quartz dust in 100 cc. of distilled water at 37.2°C. for twenty hours. This solution was filtered, analyzed colorimetrically for silica,* and then divided into two portions. To one part of the filtrate was added .1 gram of "Aluminum Bronze" powder (manufactured by Baer Bros., New York) which had been previously washed in acetone, and both parts were again agitated for twenty hours. These were filtered and analyzed colorimetrically. The analyses showed that silica had been removed from the solution containing aluminum, but had remained essentially the same in the other. The procedure was repeated with one modification—the *pH* of the solutions was kept below 5 by the addition of HCl. The silica was *not* removed since the aluminum was forming AlCl_3 instead of hydrolyzing. The procedure was repeated again allowing the aluminum a few minutes only to operate instead of twenty hours. Silica was not removed from solution. It is thus apparent that aluminum has the capacity to remove silica from nearly neutral aqueous solutions, if given sufficient time to operate.

Aluminum hydrolyzes in neutral solutions and forms $\text{Al}(\text{OH})_3$, a highly insoluble, flocculent substance which is capable of adsorbing, or chemically combining with many dissolved substances. To test the effect of $\text{Al}(\text{OH})_3$ on silica in solution, the following experiment was run: 50 cc. of a previously prepared silica solution of known concentration was made 0.01*N* in respect to AlCl_3 . This solution was neutralized with $\text{Na}(\text{OH})$, shaken for one minute, and filtered free of the precipitated $\text{Al}(\text{OH})_3$. Colorimetric analysis of the filtrate showed complete removal of the silica. A similar solution was prepared, in which the *pH* was kept below 5 to prevent formation of $\text{Al}(\text{OH})_3$, filtered and colorimetrically analyzed. There was *no* reduction in silica. Therefore, freshly precipitated $\text{Al}(\text{OH})_3$ is capable of immediately removing silica from solution. Similar tests were made with other flocculent metallic hydroxides. To prepared silica solutions of known concentrations were added soluble salts of magnesium, iron, tin, zinc, calcium and nickel, in quantity sufficient to make them 0.1*N* in respect to these metallic ions. The solutions were

* We define "dissolved silica" as that which is revealed by colorimetric analysis. This we believe gives the same meaning to the term as that of Denny, Robson and Irwin.

then made alkaline with NaOH, filtered and analyzed colorimetrically. The major portion of the silica was removed in each case. It is evident, then, that aluminum hydroxide and these other hydroxides can remove silica from solution.

Another experiment was run to show that the presence of aluminum with silica in aqueous solution has no apparent effect on the total amount of silica which dissolves. In separate flasks, one with aluminum and one without, quartz dust was agitated with water for twenty hours, filtered and analyzed colorimetrically. As before, one filtrate contained silica and the other had almost none. The two filter papers with the residues were next treated with 100 cc. each of 1.2*N* HCl and again filtered. NaOH was added to the filtrates, since the silico-molybdic acid color used in the colorimetric test for silica is not so intense in strongly acid solution. However, in order to prevent $\text{Al}(\text{OH})_3$ from precipitating, the *pH* was not allowed to rise above 5. The solution containing aluminum showed silica, the other showed very little. The silica found here had of course been released by dissolving the aluminum. Furthermore, the silica found here was sufficient to indicate equal solubility as indicated by colorimetric tests in both cases—one with aluminum, the other without. That is, the silica dissolved by water alone, as revealed in the filtrate, plus that resulting from the HCl treatment of the filter paper containing quartz alone is equal in amount to the trace in the filtrate from quartz and aluminum in water plus the larger amount resulting from the HCl treatment of the filter paper containing quartz and aluminum. It is evident, then, that the presence of aluminum does not apparently modify the amount of silica which dissolves.

RELATIONSHIP OF ALUMINUM TO PARTICULATE SILICA

Let us now examine the effect of aluminum on particulate silica and compare this effect with that of other protectors already identified.

Silica dust which has been agitated in distilled water cannot be completely filtered out to yield a clear solution by using either fine-grained paper or a thick asbestos pad in a Gooch crucible. The combined use of gravimetric and colorimetric analysis shows that the smaller portion of the silica which is present in such a solution is in the soluble form and the larger portion is in suspension. The suspended particles are in a disperse state, each with the same charge, and these will not flocculate or combine into aggregates large enough to remain on the filter medium. If a suitable substance carrying an opposite charge is added to the suspension, flocculation occurs and filtration yields a clear solution. Tests were made by adding aluminum, carbon, hematite, calcite, Portland cement and gypsum to separate portions of a cloudy filtrate of silica in water. These

solutions were shaken one minute and filtered. In each case the filtrates showed almost complete removal of the visible suspended silica. (We did not deem it necessary to make quantitative analyses.) A control without a flocculating agent was filtered a second time and showed no visible reduction. Aluminum, like these other protectors, will flocculate suspended silica.

It is generally recognized that electrolytes will bring about flocculation of disperse suspensoids, some requiring greater concentration than others. This phenomenon is discussed in any text on colloid chemistry. To test the effectiveness of flocculation by neutralization of the silica charge by that carried by a strictly particulate protector, we chose carbon, since it is insoluble in water and does not furnish ions to the solution. Cabot's lamp black was deactivated by heating in the absence of air in a platinum crucible over a Meeker burner, and then repeatedly extracted with boiling distilled water.* One gram of this carbon was agitated twenty hours at 37.1°C. with one gram of silica in 100 cc. of distilled water. A second flask with silica alone in water was run as a control. The filtrates of these flasks were analyzed colorimetrically and found each to contain 4 mg. of silica per liter of solution. Gravimetric analyses were next made and showed a reduction from 173 mg. of silica per liter of the control filtrate to 17 mg. per liter of the silica-carbon filtrate. These results emphasize the effectiveness of flocculation of particulate silica by a non-ionizing substance.

The following statement is made by Denny, Robson and Irwin—"The solubility of quartz is increased by the presence of small amounts of the carbonates—of magnesium—and calcium." This statement is true, but the obvious implication, which has already been expressed by others,⁹ is that these carbonates increase the silicosis hazard by their presence. This is based on the apparent belief that silica in solution is the cause of silicosis. On the other hand, since these carbonates carry in body fluids a charge opposite to that carried by silica particles, they tend to flocculate the silica and may thus serve as protectors. The efficacy of magnesium carbonate may be questioned on another basis—it is so much more soluble in water than calcite that it might dissolve before its protective purpose is fulfilled. This can be answered only by animal experiments for which others are better qualified.

TO RECAPITULATE

In the lung the harmful influence of silica is apparently at its peak when the silica is present as a colloid. The system is unable to handle it

* A high *pH* carbon should be used, since these are positively charged in nearly neutral solutions. All carbons are not equally satisfactory.

in this state. Our chief conclusion is that the action of a protector, whether mineral or metallic, seems to be to collect this disperse silica into unit aggregates which may be removed by phagocytosis.

Since it has been shown that aluminum does not modify the ability of silica to pass into aqueous solution, and since it has been shown that aluminum flocculates silica in suspension, aluminum is recognized as another protector of the type already described in the literature.

Still other potential protectors, more suitable than any of these for specific industrial purposes, may be selected by methods described.

We wish to acknowledge the cooperative suggestions and criticisms of Professor K. P. Link and Mr. R. Dimler of the biochemistry department, and of Professor E. Truog of the soils department of the University of Wisconsin.

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THE MARIA ELENA METEORITE

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HISTORY

The Maria Elena meteorite was presented to the United States National Museum, Washington, D. C., late in 1935, through the agency of Mr. Mark C. Bandy. The donors were Mr. Coope, Manager of the Oficina Maria Elena, Antofagasta, Chile, and Sr. Fernando Araya Valdes of the same company. Very little is known about the earlier history of this iron meteorite. It was not a witnessed fall but was found in the Chilean desert. It is reported that it was originally thought to be a mass of silver. Before its presentation to the Museum, a hole about one half inch in diameter had been drilled through the center along the shorter axis apparently for the purpose of sampling the mass.

It is catalogued at the United States National Museum as No. 1221. Three slices have been cut from the mass and two of these have been distributed to other collections as follows:

Mr. Coope, Manager, Oficina Maria Elena, Chile.....	End piece,
H. H. Nininger, Denver, Colorado.....	235 grams.

DESCRIPTION

The weight of the mass, as received by the Museum, was 15.5 kilograms. The maximum dimensions were 18.5 cm. by 23.5 cm. by 11.5 cm. It was an irregular ellipsoid with one large, rather flat face, the opposite face was well arched. The latter face apparently had been exposed to the weather and is covered with the fine pitting which is characteristic of the effect of sand blasting under desert conditions. Assuming that both faces of this meteorite were similar at the time of its fall, the part exposed to the moving sand grains has lost practically all of the features which are conspicuous on the protected face (Fig. 1). The protected flat face exhibits the original coarse pitting characteristic of meteorites. At one end of the buried face there is an unusually large and deep cavity, the dimensions of which are 7.6 cm. by 8.6 cm. by 4.5 cm. in depth. The iron is covered by a thin oxidized crust which is a little thicker in the bottom of the large cavity.

A slice, ground to a fine matte surface and etched with dilute nitric acid in alcohol, shows that the meteorite is a fine octahedrite (Fig. 2). Measurements made at random on the face, show the dimensions across



FIG. 1. Upper or exposed surface of the Maria Elena meteorite, showing the fine pitting which is the result of the sand blasting which has removed practically all the original meteoric structure. The hole, drilled for sampling purposes, is very noticeable. Two-fifths natural size.



FIG. 2. Etched slice of the Maria Elena meteorite. One-half natural size.

the kamacite grains to range from 0.1 to 0.4 mm. The majority are about 0.2 mm. It is, for the most part, kamacite with moderately abundant, very thin lamellae of taenite. Plessite areas are small, inconspicuous or wanting. Troilite is sparingly present as a few small nodules, the diameters of which are less than 3 mm., and as a few thin, short blades. Schreibersite was not recognized in any of the etched surfaces.

ANALYSIS

A piece, which weighed about 17 grams, was cut from the meteorite and the oxidized coating was ground off. One minute speck, which may have been troilite or schreibersite, was visible on the bright metallic surface but could not be identified. The specific gravity of this fragment was 7.74. It was dissolved in dilute nitric acid and aliquot portions were analyzed for the various constituents. Iron was determined both volumetrically and gravimetrically on separate samples and the nickel was determined in each of these portions. The iron in each sample was precipitated four times to remove the occluded nickel. The results of both determinations as well as the determinations of the other constituents are shown in Table 1.

TABLE 1. CHEMICAL ANALYSIS OF THE MARIA ELENA METEORITE*

Fe	94.93% (Gravimetric)	94.52% (Volumetric)
Ni	4.76	4.88
Co	0.131	(0.131)
Cu	0.010	(0.010)
P	0.052	(0.052)
S	0.029	(0.029)
C	0.007	(0.007)
Pt, etc.	Nil	(Nil)
Total	99.92%	99.63%

* Analyst: V. B. Meen.

The analysis shows that this meteorite has a low content of nickel for a fine octahedrite. This low nickel content may be referable to the not very abundant taenite which was shown on the etched surface. The low phosphorus content indicates that there is a very small amount of schreibersite present, although none was recognized in the examination with the binoculars.

ACKNOWLEDGMENTS

The writer is indebted to the Assistant Secretary of the United States National Museum for the permission to use the laboratory and other

facilities of the Museum for these investigations. The assistance of Dr. W. F. Foshag and Mr. E. P. Henderson of the United States National Museum, and Dr. J. P. Marble was greatly appreciated.

NOTES AND NEWS

OCCURRENCE OF WAVELLITE, GILES COUNTY, VIRGINIA

LENA C. ARTZ,
Arlington, Virginia.

The specimens of wavellite described below were collected approximately one mile northeast of Kern post office, along Big Stony creek, Giles County, Virginia, during July 1938. The mineral occurs in red sandstone of Clinton age as incrustations on joint planes. The sandstone

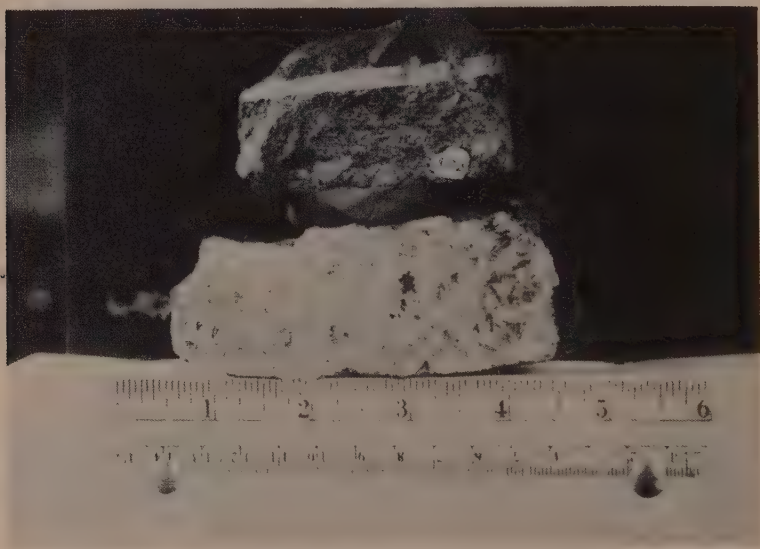


FIG. 1. Wavellite, upper photograph showing the thin incrustation in a joint plane, and lower the radiated mineral. Photo by Jos. K. Roberts.

is colored red to brownish red by iron oxides, and its Niagaran age is indicated by its fossil content. Wavellite is not at all a common mineral in Virginia or elsewhere, and only small amounts were collected at this one locality in Giles County.

The mineral occurs in radiated, fibrous form, and individual fibers attain as much as 1 cm. in length (Fig. 1). Some of the incrustations are as much as 4 mm. thick, but usually much thinner. The mineral aggre-

gates are white in color with a pearly to vitreous luster, and the fibers are translucent to transparent. The mineral gives the usual test for phosphorus with nitric acid and ammonium molybdate. In the field it might be mistaken for a zeolite, except for its association with sandstone.

The indices of refraction are nearly those of the wavellite described recently by F. Ulrich (*Min. Abs.*, II, 1923, p. 141). It is optically positive, $2V = 70^{\circ}-75^{\circ}$; the indices determined by the immersion method with white light are as follows: $\alpha = 1.530$, $\beta = 1.540$, and $\gamma = 1.558$; $B = 0.028$, dispersion distinct, $r > v$, and $Z = c$ axis. The high indices are probably due to the presence of iron. There are no indications of hydrothermal action and while the origin of the wavellite is apparently secondary, the writer offers nothing towards the particular mode of genesis. Gratitude is hereby expressed to Miss Jewell J. Glass, U. S. Geological Survey, who made the physical measurements. The specimens are in possession of the Biological Station of the University of Virginia at Mountain Lake, Giles County, Virginia.

PROCEEDINGS OF SOCIETIES

MINERALOGICAL SOCIETY OF SOUTHERN CALIFORNIA

(Extracts from the annual report of the President, June 18, 1938)

On this seventh anniversary of the founding of the organization, I shall simply summarize the events of the current year.

In September, 1937, Buel Hunt of the U. S. Forest Service exhibited two films teaching the importance of conservation of our chaparral, and the necessity of erosion control. In October, Dr. William C. Putnam of Los Angeles Junior College gave an illustrated lecture on the geology and mineralogy of the Mono Craters. In November, Dr. Ward Smith of Pomona College taught us the preparation and use of thin sections of rocks. In December, Donald Curry, geologist of the Death Valley National Monument, told us of his area's geologic and historic background. The feature evening of the year was on January the tenth when we were honored by the presence of the well-known mining engineer, Dr. Louis D. Ricketts, who spoke on his work at Ajo, Arizona. His address was illustrated with motion pictures. In February, Dr. John H. Maxson of the California Institute of Technology, spoke on "Mineral Development in Siberia." In March, Alfred Livingston of Los Angeles Junior College gave us convincing proof that our Southern California beaches were in imminent danger of destruction. Through the courtesy of the Union Oil Company, our April program consisted of two fine geological motion pictures. In May, Major Julian Boyd, consulting engineer for the Pacific Coast Borax Company, gave us the benefit of his wide knowledge of gold mining. Tonight we had the pleasure of enjoying the remarkable colored motion pictures taken by Charles Heald on the Society's last two nine-day excursions into Arizona and Nevada.

Our first and largest excursion of the year was on Sunday, October 17, to Soledad Canyon, Vasquez Rocks and vicinity, with the surprising number of 90 cars and 300 people in attendance. Excellent titaniferous magnetite, ilmenite, borax ores, geodes, etc., were obtained by all. On Armistice Day, November 11, a much smaller group collected Cretaceous fossils in the Santa Ana Mountains. A most successful overnight trip was held on Novem-

ber 20-21. We visited the El Paso Mountains, Red Rock Canyon, the gold mines and mills in the vicinity of Mojave, and collected much fine polishing material at Gem Mountain. The trip to Coso Hot Springs in the early Spring netted a fine supply of obsidian, cristobalite, fayalite, sulfur, and other interesting materials. The outstanding trip of the year was the nine-day excursion in Easter week to Nevada and Arizona. On May eighth, Drs. Hoyt S. and H. Rodney Gale led thirty-six cars to Frazer Mountain, where fine collecting was enjoyed in a region of very great geological interest. The last trip of the year sponsored by the Society was the National Rocks and Minerals Outing to Big Bear Lake and Holcomb Valley on May 30th.

EDWIN V. VAN AMRINGE, *President*

NEW MINERAL NAMES

Chacaltaita

MARJA KALOCZKOWSKA: Chacaltaita, a new mineral from Bolivia. *Sprawozdania z posiedzeń Towarzystwa Naukowego Warszawskiego*, vol. 29, pp. 1-3, 1936. Polish with French summary.

ST. J. THUGUTT: Pinite from Chacaltaya, Bolivia. *Archiwum Mineralogiczne*, Warsaw, vol. 12, pp. 58-63.

A green pinite from the Caboceras mine, Chacaltaya, Bolivia, has been described by Thugutt. SiO_2 46.25, Al_2O_3 31.89, Fe_2O_3 1.52, FeO 2.08, MnO 0.15, CaO 0.29, MgO 1.00, K_2O 10.18, Na_2O 1.15, $\text{H}_2\text{O}-$ 0.12, $\text{H}_2\text{O}+$ 4.93, F 1.39. Sum 100.95.

On the basis of a variation of the unit cell from two other muscovites examined and on several lines in the x-ray photographs peculiar to it, Kaloczowska names it chacaltaita.

W. F. FOSHAG

Picroamosite

D. R. SERDUČENKO: Picroamosite—a new mineral. *Bull. Acad. Sci., U. S. S. R., Cl. Sci., Math. Nat., Ser. Geol.*, pp. 689-696, No. 5, 1936.

CHEMICAL PROPERTIES: A silicate of magnesium and iron: $(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_3$. SiO_2 55.90, Al_2O_3 1.13, Fe_2O_3 8.28, FeO 0.68, MnO 0.49, CaO 0.94, MgO 29.26, $\text{H}_2\text{O}+$ 3.20, TiO_2 , K_2O , Na_2O , $\text{H}_2\text{O}-$ tr. Sum 99.88.

PHYSICAL AND OPTICAL PROPERTIES: Color greenish gray, sometimes brownish gray. Fibrous or radially fibrous. Biaxial; $2V=87^\circ$, lies in the plane of $\{010\}$. Extinction parallel. $\alpha=1.626$ (colorless), $\beta=1.638$, $\gamma=1.651$ (light grayish brown).

OCCURRENCE: Found in blocks in a talcose rock on the banks of the Malaya Laba River, North Caucasus.

W. F. F.

Karachaite

N. E. EFREMOV: Karachaite—A new mineral. *Bull. Acad. Sci., U. S. S. R., Cl. Sci. Mat. Nat., Ser. Geol.*, No. 6, pp. 921-928, 1936. English summary.

NAME: From the locality Karachi, Northwestern Caucasus.

CHEMICAL PROPERTIES: A hydrous silicate of magnesium, H_2MgSiO_4 . Analysis: SiO_2 47.12, Al_2O_3 2.82, Fe_2O_3 2.58, MgO 30.90, CaO 3.20, $\text{H}_2\text{O}+$ 13.48, $\text{H}_2\text{O}-$ 0.76. Sum 100.86.

PHYSICAL AND OPTICAL PROPERTIES: Color yellow, luster silky. Fibrous. $G=2.20$. Elongation positive; extinction parallel. $\alpha=1.542$, $\gamma=1.546$.

OCCURRENCE: Found in the asbestos deposits at Shaman-Beklegen, Karachai, Northwestern Caucasus.

W. F. F.

Asovskite

N. E. EFREMOV: Asovskite—A new mineral from the group of hydroferriphosphates. *Trans. Lomonosov Inst. Acad. Sci., U. S. S. R.*, vol. 10, pp. 151–155, 1938. Russian with English summary.

NAME: From the locality, shore of the Azovsky (Azov) Sea.

CHEMICAL PROPERTIES: A hydrous ferriphosphate, $3\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. Analysis: Fe_2O_3 52.73, Mn_2O_3 1.68, P_2O_5 15.90, FeO None, CaO 2.84, MgO trace, SiO_2 2.64, CO_2 0.15, SO_3 none, $\text{H}_2\text{O}+$ 11.87, $\text{H}_2\text{O}-$ 11.28. Sum 99.09. Easily soluble in HCl and HNO_3 but with difficulty in concentrated H_2SO_4 .

PHYSICAL AND OPTICAL PROPERTIES: Color dark brown; streak brown. Luster tarry. Fracture conchoidal. $H.=4$. $G.=2.5$. Slightly birefringent, n about 1.758.

OCCURRENCE: Found as reticulating veinlets filling fissures in iron ores of Taman.

W. F. F.

"Kratochirlite"

R. ROST: The minerals of the burning heaps in the vicinity of Kladno, *Rozpravy. Česká Akademie, Kl II*, vol. 47, No. 11, 1937.

Among the organic compounds formed by the distillation from the combustion of coal dump heaps is the hydrocarbon $\text{C}_{13}\text{H}_{10}$ (Fluorene). $\alpha=1.557$, $\beta=1.725$. Other compounds formed are α and β sulfur, γ selenium, tschermigite, epsomite, lapparentite, mascagnite and letovicite.

W. F. F.

Foschallasite

PETER CHIRVINSKY: Foschallasite from the Chibina Tundra. *L'Academie des Science de l'U. S. S. R.*, pp. 757–763, 3 figs., German summary.

NAME: From its relationship to foshagite and centrallasite.

CHEMICAL PROPERTIES: A hydrous silicate of calcium: $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. Analysis (by Starynkewitsch-Bornemann) SiO_2 32.65; R_2O_3 1.89; CaO 45.45; Na_2O 0.40; H_2O 0.16; Ign. loss 16.66. Sum 97.21.

CRYSTALLOGRAPHIC PROPERTIES: Orthorhombic or monoclinic; tabular to $\{100\}$, elongated along $\{100\}$ $\{010\}$, striated parallel to $\{100\}$ $\{010\}$.

PHYSICAL AND OPTICAL PROPERTIES: Color snow-white. $H.=2\frac{1}{2}$ –3. $G.=2.5$. Cleavage $\{100\}$, perfect. Biaxial negative, $2V=12^\circ$ – 18° .

OCCURRENCE: Found as thin plates, sometimes radially aggregated, forming veins in the Lovtschorrit mine at Yukspor, associated with calcite and mesolite.

W. F. F.

Omission

In the description of *thioelaterite* on page 542, August 1938, "S 2.96" was omitted from the chemical analysis.

NEWS

Roland B. Snow has become a research engineer at Battelle Memorial Institute, Columbus, Ohio, and has been assigned to work on ceramics problems. For the past two years he has been petrographer on the research staff of Carnegie-Illinois Steel Corporation, South Chicago, Illinois.

The Geological Society of America is carrying on a special program of public education in geology. In connection with this program the officials of the Society are interested in securing information regarding scientific progress in mineralogy. Members of The Mineralogical Society of America carrying on programs of research which may be of interest to the general public will aid this program considerably if they will send notices of their investigations to the secretary's office. It is particularly desirable to have advance notices of subjects to be presented at the Annual meeting.

Dr. James Gilluly of the U. S. Geological Survey has recently been appointed Chairman of the Department of Geology, University of California, Los Angeles, California.